Abstract—Vanadium dioxide (VO₂) is a phase transition material which undergoes a reversible metal-insulator transition (MIT) when triggered by thermal, photo, electrical, and even stress. The huge conduction change of VO₂ renders it a promising material for terahertz (THz) manipulation. In this paper, some interesting works concerning the growth and characteristics of the VO₂ film are selectively reviewed. A switching of THz radiation by photo-driven VO₂ film is demonstrated. Experiments indicate an ultrafast optical switching to THz transmission within 8 picoseconds, and a switching ratio reaches to over 80% during a wide frequency range from 0.3 THz to 2.5 THz.

Index Terms—Active device, phase transition; terahertz (THz), vanadium dioxide.

1. Introduction

The terahertz (THz) technology offers a variety of applications including spectroscopy, imaging, and communications. Much effort has been devoted to developing THz sources and detectors, which has promoted THz research into one of the most rapidly growing field. However, substantive progression of THz applications also depends on the realization of active components for wave manipulation and modulation[1]. Lying between the radio frequency and infrared, THz electromagnetic waves have been notoriously difficult to modulate because many materials inherently do not respond to THz radiation. High-performance elements to control and manipulate THz electromagnetic waves, such as modulators, switches and active filters are in high demand to develop sophisticated THz communication and imaging systems[2],[4].

Vanadium dioxide (VO₂) is the interesting electron material that exhibits a reversible first-order phase transition from a insulating state to a metallic state[5]–[7]. Associated with this metal-insulator transition (MIT) are a lattice structural transition from the monoclinic to tetragonal, a change of conductivity by several orders of magnitude, and significant changes of the optical properties at all wavelengths[8]–[10]. These properties render VO₂ a promising candidate for a variety of interesting applications, such as the electronic switch, gated field effective transistor (FET), memories, modulators, thermal, and chemical sensors. Experimental and theoretical studies to unravel the mechanism of MIT have been ongoing for nearly half a century. A number of reviews on MIT mechanisms and materials in the past years indicate the consistent interest in this subject[11]–[13]. A recent review gave a detailed description to the representative device concepts utilizing MIT in VO₂ films[14]. The VO₂ film plays an especially important role in the technologically relevant THz frequency regime[1],[15]. Since semiconductors are transparent to THz wave while conductors are reflective, the THz transmission can be dynamically modified from transparent to reflecting modes by controlling the phase transition of the VO₂ film. VO₂ films, separately or integrated with resonant element (e.g. metamaterials), have already been used to control and manipulate the THz wave[16]–[20].

2. Fabrication of High Quality VO₂ Films for THz Application

For either separate or integrated applications, high quality VO₂ films with strong response to THz radiation are fundamentally needed. VO₂ films have been fabricated by sol-gel[16], reactive sputtering[21],[22] or pulsed laser deposition (PLD)[23] techniques on a variety of substrates, including sapphire, TiO₂, silicon, glass, and fused silica. The crystal structure, oxide phase, crystallinity, grain size, and phase transition characteristics can be strictly controlled by optimizing the growth process.

One interesting work is that a polymer-assisted-deposition (PAD) method was proposed to fabricate vanadium oxide thin films on sapphire[24]. PAD is a chemical solution deposition technique. Besides the advantages of low cost, easy setup, and the ability for large area coating, PAD shows its unique ability in the precise
control of both structures and stoichiometry of thin films. By using the PAD technique, VO₂ films with controllable crystal phases were synthesized on (0001) sapphire substrates by modifying the processing parameters. Microstructural studies from X-ray diffraction and high-resolution transmission electron microscopy reveal that the monoclinic VO₂ films have good crystallinity and epitaxial quality, as shown in Fig. 1 (a) to Fig. 1 (c). The interface relationships between the films and the substrates were determined to be VO₂[001]//Al₂O₃[0001] and VO₂[010]//Al₂O₃[112̅0], respectively. The temperature dependence measurements of electric resistivity shown in Fig. 1 (d) and (e) indicate that the metal-insulator-transitions for VO₂ thin films occur at 341 K, with a change of four orders of magnitude in resistivity. The transition temperature width of VO₂ film is as narrow as 5 K. The properties of the as-grown VO₂ film by PAD is comparable to that of the epitaxial film grown by PLD, indicating that PAD is a feasible way to synthesize high quality vanadium oxide films.

Fig. 1. Structure and phase transition properties of the VO₂ film grown by PAD technique: (a) XRD φ-scan result of a VO₂ thin film on Al₂O₃ (0001) substrate, (b) cross-sectional high resolution TEM images from VO₂ on Al₂O₃ (0001) substrate, (c) corresponding SAD pattern from VO₂ and substrate, (d) resistivity versus temperature curves for a VO₂ thin film grown on Al₂O₃ (0001) substrate, and (e) Gaussian fitting of the resistivity versus temperature curve for the VO₂ thin film.

To fabricate high quality VO₂ thin films, Al₂O₃ and TiO₂ are conventional employed as substrates. The epitaxial growth of the VO₂ thin films on sapphires renders a change of the resistivity (ΔR) more than four orders of magnitude due to the very small lattice mismatch [24]–[26]. However, Al₂O₃ and TiO₂ are expensive. A cost-effective substrate is silicate glass. However, silicon glass has a huge absorption to THz wave thus it is not a good choice in the THz area. We thus proposed a new kind of glass substrate—BK7 glass, which is highly transparent to both THz and optical bands thus is suitable for THz applications. By using the low temperature magnetron sputtering technology, high quality VO₂ films were deposited on the BK7 substrate without post-annealing treatment. The crystallinity and microstructure of the thin film were investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM). The results indicate that the as-deposited film crystallizes directly to single-phase VO₂ with (011) preferred orientation and compact nanostructure. Under a heating-cooling cycle, films undergo a metal-insulator transition with an abrupt change in resistivity more than 4 orders of magnitude. THz transmission modulation was characterized by a THz time domain spectrum system (THz-TDS). The results are plotted in Fig. 2. It can be seen that the film exhibits a broadband modulation to THz wave from 0.2 THz to 2 THz with a giant modulation depth of 89%. Due to the high transparency and the huge modulation effect, the VO₂/BK7 sample can be widely used as THz devices such as modulators and switches.

Electrically triggered phase transition (E-MIT) in VO₂ is of great interest in novel devices for electric switches, resistance random access memory (ReRAM) networks, and so on [27]–[30]. Out-of-plane metal-VO₂-semiconductor (MOS) structures set the basis for realization of E-MIT in VO₂ [31]–[34]. In this vertical device geometry, TiO₂ and sapphire are insulating and may not be applicable as the bottom contacts in VO₂ based out-of-plane devices. To date, the most frequently used conducting substrate in vertical VO₂ devices is heavily doped Si, which is the mainstay substrate material in the microelectronics industry [32], [33], [35]. However, the large crystal lattice mismatch and formation of silicides or native oxide layers set big obstacles for directly depositing VO₂ on the Si substrate [36], [37]. The direct deposition of VO₂ on the Si substrate can only render a two orders change in the resistivity of the VO₂ thin film and a thermal hysteresis (ΔH) of more than 20 K [38]. Such buffer
layers as yttria stabilized zirconia (YSZ) film were proposed to improve the growth of VO₂ thin films on the Si substrate\(^\text{[39]}\). It was reported that the 145 nm YSZ buffer layer can greatly decrease the thermal hysteresis (ΔH) to 6 K and increase the ΔR to 3 orders of magnitude\(^\text{[39]}\). However, due to the thermal instability in phase and microstructure of YSZ material, novel techniques for fabricating high quality VO₂ thin films on the silicon substrate are still highly desirable.

Fig. 2. Temperature dependence of the THz transmission through VO₂/BK7 sample: (a) the time domain spectrum, and (b) the frequency domain spectrum.

Heavily doped Ge substrates are conducting, and have a slightly smaller lattice mismatch with VO₂ than Si, thus have been proposed as the substrate for VO₂ based vertical devices. By physical vapor deposition, high-quality VO₂ thin films have been successfully grown on single crystal Ge(100) substrates\(^\text{[34]}\). It was reported that the VO₂ thin films grown on the Ge substrate show a higher degree of crystallinity, slightly reduced compressive strain, and larger resistance change across MIT compared to those grown on the Si substrate. Voltage-triggered MIT is observed at room temperature at a critical voltage of only 2.1 V with a hysteresis window of \(1 \text{ V}\) in VO₂ thin films grown on Ge. Ge may be a suitable substrate for further explorations of phase transition based oxide electronics utilizing MITs.

Fig. 3. I-V character curves of VO₂ based MOIM structure: (a) current-voltage (I-V) curves of the test circuit at various temperatures in a heating process with the singal sweeping mode; inset: the schematic diagram of the MOIM structure, the double sweeping mode at particular temperature of \(25^\circ \text{C}\) and the leakage current I-V curves of the test circuit for the deposited buffer layer SiO₂. (b) and (c) the ln (I/V) vs. Sqrt (V) constructed from I-V curves at various temperatures shown in (a); inset in (b) the magnified region of the ln (I/V) vs. Sqrt (V).

It was recently reported that with particular perpendicular structures, for example the metal/VO₂/metal structure, the device size can be significantly reduced to submicron scale and the OFF (insulating state)/ON (metallic state) switch time can be improved to less than 2 ns\(^\text{[31]}\). The ultrafast E-MIT is believed to be induced by electronic correlation effects rather than the joule heating, because the heating driven MIT would give rise to a longer switch time\(^\text{[40]}\). However, the current-driven joule heating effect in a metal/VO₂/metal structure is inevitable once the metallic state of VO₂ is established, which will hinder the ON-OFF process of the device. In order to eliminate this joule heating effect, a metal-oxide-insulator-metal (MOIM) structure has been demonstrated by introducing a thin SiO₂
insulating layer between the VO₂ film and the bottom metal layer[41]. By the reactive sputtering method, the VO₂ film has been successful grown on SiO₂ buffered metal electrode, and a metal-oxide (VO₂)-insulator(SiO₂)-metal (MOIM) junction has also been fabricated. The VO₂ film has an abrupt thermal-induced MIT with a change of resistance of 2 orders of magnitude. The electrically-driven MIT (E-MIT) switching characteristics have been investigated by applying a perpendicular voltage to the VO₂ based MOIM device at particular temperatures, sharp jumps in electric currents were observed in the I-V characteristics under a low threshold voltage of 1.6 V, as indicated in Fig. 3. With the SiO₂ layer, the current value is smaller than 0.1 A both before and after the MIT of VO₂, thus the Joule heating effect can be depressed. Furthermore, the SiO₂ buffer layer can eliminate the stress between VO₂ films and the metal electrode, thus can improve the quality of VO₂ films. SiO₂ has excellent thermal, mechanical, and optical properties, and is compatible with micro-electromechanical devices, which have a great application in the semiconductor process. This MOIM structure is expected to be of significance in exploring ultrafast electronic devices incorporating the correlated oxides based MOIM structure.

3. Broadband THz Switching Based on Photo-Induced Phase Transition in Vanadium Dioxide Films

By thermally triggering the phase transition of these films, a large switching ratio to THz radiation can be achieved during a broad frequency range. However, for the thermal control, the switching speed is essentially restricted to the time of the heat dissipation, which is in the second scale[20]. Moreover, for electrical control, the voltage applied to the gate terminal is several tens of volts, which can deteriorate the reliability and durability of the switching devices and give rise to considerable switching power loss[42]. It was reported that the photo-induced phase transition is remarkably fast due to a nonthermal mechanism[43]. Nakajima et al.[44] observed a picosecond THz transmission switching by using 8mJ/cm² pulse laser to pump the VO₂ thin film, but the magnitude of the THz transmittance change is only 36.8%. Broadband, ultrafast response time, and large switching ratio are still not achieved for the VO₂ based THz optical switching. In this work, by using the above-mentioned VO₂/BK7 sample, the photo-induced phase transition and the corresponding THz transmission modulation were demonstrated.

The temperature dependence of electric resistivity for the as-prepared VO₂ films was measured by a four-point probe method, as shown in Fig. 4. The resistivity changes are as large as four orders of magnitude during the phase transition. The transition temperatures can be deduced by Gaussian fitting of the resistivity versus temperature curves (the inset in Fig. 4). The transition temperature is 64.4 °C for heating, and 60.5 °C for cooling. It should be noted that the transition width (ΔT) is only 3.5 K for the as-grown VO₂ film, which is comparable to that of the epitaxial film grown by pulse laser deposition technology[25].

We determined the photo-induced MIT of the thin VO₂ films by THz pump-probe technology. The pump-probe measurement was performed by using a Ti:sapphire regenerative amplifier delivering ultrashort optical pulses with a duration of 100 fs and a central wavelength of 800 nm at a repetition rate of 1 kHz. The electro-optic detection method was chosen to measure the transmitted signals. The output of the laser has an average power of 0.9 W, and is divided by beam splitters into three portions (pump, generation, and probe). The spot size of the pump laser is enlarged to 8.0 mm in diameter, and the average pump power is 18 mW, corresponding to a pulse energy of 143 μJ/cm². The picosecond time resolution is provided by delaying the pump-probe arrival time at the sample. Fig. 5 (a) and Fig. 5 (b) show the time domain waveforms of the THz signals transmitted through the bare BK7 substrate and BK7+VO₂ film in the presence and absence of optical pump. It can be noticed that the THz signals for the bare BK7 substrate are almost identical regardless of the optical pumping, indicating that the BK7 glass has no response to THz wave. On the contrary, the amplitude of the transmitted THz wave through the VO₂ film on BK7 substrate is reduced significantly by the optical pump with a little shift of the peak position. This slight position-shift means a small decrease of the refractive index of the thin film with optical pump.

In Fig. 5 (c) we plot the spectrum obtained by conducting the Fourier transformation to the time-domain data plotted in Fig. 5 (b). Since the THz-TDS measurements were performed in the atmosphere, a few strong absorptions by vapor were clearly observed in the frequency spectrum. By normalized to air reference, the transition spectrum of VO₂ thin films was obtained and
plotted as Fig. 5 (d). It can be seen that the VO$_2$ thin films, with the substrate, have a high transmittance of about 70%, while the optical pump reduces the THz transmittance to about 10%. Therefore, we obtain an average transmission modulation depth larger than 80% in the frequency range from 0.3 THz to 2.5 THz. This modulation depth is comparable to that of the thermal-induced THz transmission modulation, which is much higher than the previously reported photo-induced THz modulation and the metamaterials based modulator.

![Graphs](image)

**Fig. 5.** Time traces for transmitted THz waves through (a) bare substrate, (b) VO$_2$ films on substrate with and without laser pump, (c) frequency spectrum using the Fourier transformation to the time-domain data plotted in (b), and (d) the transition spectrum of VO$_2$ thin films.

The photo-induced switching time of our sample was also studied by using the THz pump-probe method. The THz peak transmission was measured by changing the relative time delay between the THz wave and the optical pulse. Fig. 6 shows the temporal evolutions of the transmittance changes of THz wave for VO$_2$ films. The transmittance drops rapidly just after the photoexcitation, and reaches the minimum value within 8 ps. The 90% to 10% transmission switching time we obtained is about 6 ps, which is significantly fast than the thermal-induced THz switching\[20\]. The reversal process of the phase transition is longer beyond the limitation of our set-up, which is estimated to be from a few nanoseconds to hundreds of nanosecond depending on the pump intensity. Remarkable features of the switching behavior investigated here include the room-temperature operation, broadband and ultrafast response, and larger switching ratio. Moreover, the 143 μJ/cm$^2$ pump threshold for the photoinduced phase transition is equivalent to a 75 pJ pulse for a typical 50 mm$^2$ mode size in a single-mode fiber, making such schemes attractive for real-world applications.

![Graphs](image)

**Fig. 6.** Pump–probe signal as a function of pulse delay measured at room temperature.

### 4. Conclusions

In this paper, we selectively review some recent work on the fabrication and exploration of high quality VO$_2$ phase transition films for THz manipulation. The ultrafast nature of the phase transition along with spectacular
changes in the electrical/dielectric properties creates several possibilities for THz modulation devices such as modulators, and switches. The VO₂/BK7 sample was used to demonstrate its photo-induced phase transition and the corresponding THz transmission switching. It was found that by pumping the VO₂ film with relatively lower laser power, the picosecond switching time, large modulation depth, and broad bandwidth properties were simultaneously achieved. VO₂ based high-performance elements to control and manipulate THz electromagnetic waves are excellent candidates to develop sophisticated THz communication and imaging systems.

References


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