引用格式：WANG Zixin, DONG Ningning, WANG Lulu, et al. Femtosecond Laser Induced Optical Property Transition of Vanadium Dioxide (Invited)[J]. Acta Photonica Sinica, 2022, 51(10):1014007
王梓鑫,董宁宁,王路路,等. 飞秒激光诱导二氧化钒光学特性转变(特邀)[J].光子学报,2022,51(10):1014007

飞秒激光诱导二氧化钒光学特性转变(特邀)

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摘 要:为研究激光诱导对二氧化钒光学性质的具体影响,采用磁控溅射技术制备了二氧化钒薄膜。利用原子力显微镜和X射线衍射仪对样品进行表征,发现其具有良好的平整度及致密均匀的结构,是纯相二氧化钒(M)薄膜,并且在透过率-温度变化曲线中观察到了典型的热滞回线。采用透/反射强度扫描系统研究了二氧化钒薄膜的光学特性,实验结果表明,在飞秒激光诱导下样品经历了非线性吸收过程、相变过程、稳态过程和损伤过程,非线性吸收过程由双光子吸收效应主导而相变过程与激光热效应息息相关。进一步研究发现,随着激光重复频率增加,增强的热效应导致其相变开启阈值和损伤阈值明显下降。

关键词:二氧化钒;飞秒激光诱导;半导体-金属相变;非线性光学;透/反射强度扫描
中图分类号:O436 **文献标识码**:A **doi**:10.3788/gzxb20225110.1014007

0 引言

金属氧化物中的半导体-金属相变由于其在凝聚态物理中的科学意义及其在多种应用中的可能性而备受关注。在过去的近半个世纪,有关相变机制的实验和理论研究从未停止[1-6]。其中二氧化钒(Vanadium Dioxide,VO_2)由于~68 ℃下的相变特性而备受关注[7],它是一种具有重要基础研究和实用价值的独特材料。VO_2相变可以通过多种激励触发[8,9],其光学性质变化明显,因此被广泛应用于光开关[10-12]、智能窗[13,14]、光存储[15]和激光防护[16,17]等领域。

自1959年MORIN F J[7]发现VO_2的相变特性以来,VO_2就成了相变材料研究的热点。这种相变是可逆的、非破坏性的,属于一级相变。在外界条件刺激下,VO_2由单斜半导体相($P2_1/c$空间群)向四方金红石金属相($P4_2/mnm$空间群)转变,伴随着大约四个数量级的电阻变化,其光学性质也随之改变[18-21]。从四方相到单斜相的恢复过程中,晶格结构发生畸变,V^{4+}发生空间位移,V^{4+}-V^{4+}由等距离排列变为长短交替排列,导致晶胞体积增大了一倍。结构重排导致电子能带结构的变化。在四方相中,半充满的$d_{//}$带与π*带部分重叠,费米能级落在两带之间,表现为金属性质。由四方相向单斜相相变过程中,由于V^{4+}的空间位移,$d_{//}$分裂为反键$d_{//}$*和成键$d_{//}$两个带,π*带上升$d_{//}$带下降,两带之间形成了一个0.6~0.7 eV的禁带,费米面恰好落在其中,表现为半导体性质[22]。

诱导半导体-金属相变的常用方法是热触发[23,24]。在相变温度以下,VO_2为半导体相,对光具有较高的透过能力,当温度加热到68 ℃以上,VO_2由半导体相转变为金属相,其光学性质比如折射率、透射率、反射率等发生突变,对光具有较强的屏蔽作用。由于电子-电子关联和电子-晶格相互作用都对相变动力学有贡献,所以关于半导体-金属相变主要驱动力的机制仍在讨论中[25-30]。Mott理论认为VO_2相变是由电子-电子

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收稿日期:2022-08-16;**录用日期**:2022-09-19

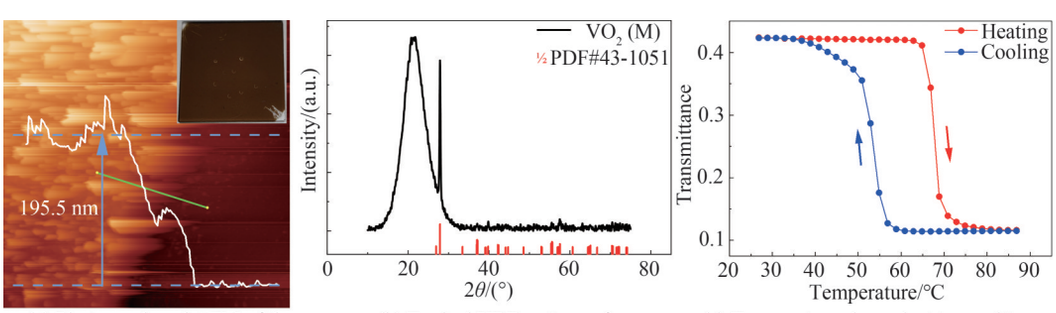
相互作用主导，当材料中电子载流子浓度超过临界载流子密度时，引起半导体-金属相变；而根据Peierls理论，由于材料晶格结构的变化，相变也可以从电子-声子相互作用中发生。VO_2相变的主导因素是结构变化还是载流子诱导，决定了VO_2是Peierls相变还是Mott相变。

诱导相变的其他方法包括激光[31-33]、电场[20]、磁场[34]、应力[35]等。在某些情况下，两个或多个激励的组合可以导致相变开启阈值的改变。特别地，在飞秒激光诱导下，相变可以在亚皮秒时间尺度上触发，由于激光诱导相变极高的响应速率和显著的光学特性变化，研究激光诱导下的相变过程具有重要意义。早在1970年ROACH W R等就利用激光诱导VO_2产生了半导体-金属相变[33]。2001年CAVALLERI A等采用X射线衍射等手段，证明了VO_2薄膜可以在小于500 fs的时间尺度内发生相变[36]。2014年MORRISON V R等利用超快电子衍射技术发现激光作用VO_2后会立即产生一个不稳定的单斜金属态[37]。关于VO_2相变过程和机制的研究始终是科研人员不懈追求的目标。

如上所述，激光诱导下VO_2发生相变时能带结构的改变会导致其光学性质的明显变化。然而在VO_2发生相变前，由于半导体固有的非线性光学性质，在激光作用下的电子跃迁会导致光学性质的改变[38, 39]。除了激光诱导VO_2相变过程的理论和实验，研究激光诱导VO_2光学性质变化的整个过程，包括透过率、反射率和吸收率随激光光强的变化关系对进一步理解包括相变在内的光响应具有重要意义。利用光学手段在超快时间尺度内实现VO_2相变控制，将有利于其在存储器件、超快光开关和双稳态光电子器件等方面的潜在应用。

1 二氧化钒的制备和表征

磁控溅射技术是物理气相沉积的一种，由于沉积速率高、成膜均匀、重复性高、适合大面积制备被广泛用于VO_2薄膜的合成[40]。本实验中，使用2 cm×2 cm的石英玻璃作为衬底，靶材选择V_2O_3陶瓷靶，采用直流反应磁控溅射系统制备VO_2薄膜。在溅射前，将衬底依次在丙酮、乙醇及去离子水中超声清洗，并用氮气吹干。溅射过程中，利用机械泵和冷泵将反应室真空度抽至10^{-4} Pa，之后将纯Ar气和Ar/O_2(3% O_2)混合气同时通入反应室中，气体比例为7∶3，气压维持在1 Pa左右，直流电源功率200 W。同时，溅射过程中样品托盘不停转动以保证薄膜制备均匀。最后，将制备的薄膜进行后退火处理，退火温度为450 ℃，真空度为0.67 Pa，退火时间为5 min，最终获得所需的VO_2薄膜样品。图1(a)为制备的VO_2薄膜，原子力显微镜(Atomic Force Microscope，AFM)图像清晰地展示了样品的表面形貌，可以发现薄膜表面致密均匀并保持了较高的平整度，样品厚度为195.5 nm。采用X射线衍射仪(X-ray Diffraction，XRD)对样品进行分析，结果如图1(b)。可以看出，在$2\theta = 40^\circ$出现了一个明显的衍射峰，对应(001)晶面，表明样品结晶度较好，为纯相VO_2(M)(JCPDS card no. 72-0514，$P2_1/c$，$a = 0.574$ nm，$b = 0.452$ nm，$c = 0.538$ nm，$\alpha = \gamma = 90^\circ$，$\beta = 122.61^\circ$)。图1(c)为测得的$VO_2$薄膜在1 036 nm透过率随温度变化关系曲线，可以看出随着温度增加VO_2薄膜在68℃附近发生半导体-金属相变，在相变温度附近透过率变化最明显，从42.1%急剧下降到11.6%，降温过程中样品在53 ℃附近从金属相恢复到半导体相，热滞回线宽度约为15 ℃。



(a) Photograph and AFM of the VO_2 film　(b) Typical XRD pattern of the VO_2 film　(c) Temperature-dependent transmittance at 1036 nm

图1 二氧化钒薄膜样品的表征

Fig. 1 Characterization of vanadium dioxide film

2　飞秒激光诱导二氧化钒薄膜的光响应

如图2所示，利用自主搭建的透/反射强度扫描装置研究了飞秒激光诱导下VO_2薄膜的光响应特性。激光器波长为1 036 nm，脉宽为650 fs，重复频率可调。通过电动衰减片实现激光能量的连续调节，激光脉冲经分光镜分为两束，一束作为参考信号由探测器PD0收集信号，另一束通过透镜（f = 200 mm）进行聚焦，样品放置在透镜焦点位置处，光斑直径为～79.7 μm，样品的透射信号和反射信号分别用探测器PD1和PD2进行测量。

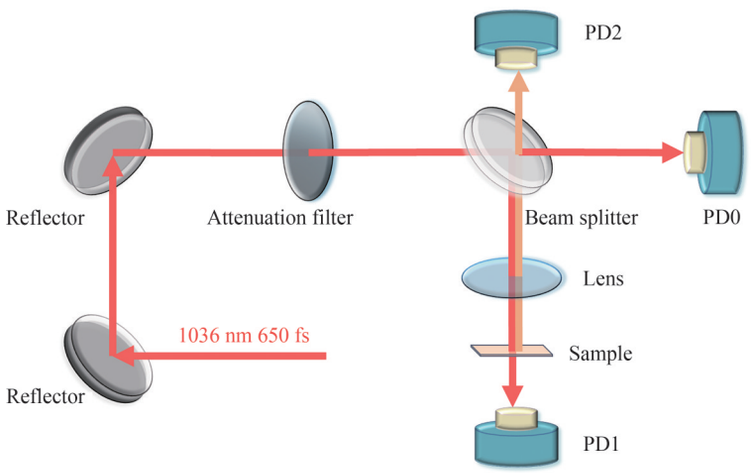


图2　透/反射强度扫描实验装置

Fig. 2　Transmission/reflection I-scan experimental setup

2.1　飞秒激光诱导二氧化钒光学特性

为研究飞秒激光诱导下VO_2光学特性的变化，测试了VO_2薄膜在激光重频为50 kHz下的透反射信号。如图3(a)所示，随着入射激光强度的增加，样品透过率和反射率变化表现为四个不同的阶段。在较低激光强度（小于26.2 mJ/cm^2）下，VO_2薄膜保持着较高的透过率，随激光强度的增加表现出从43.9%到40.3%的轻微下降，而反射率基本在6.3%保持不变，此时样品没有发生相变，仍为半导体相。这种变化主要归因于VO_2半导体的双光子吸收过程[41, 42]，电子通过吸收两个全同光子发生跃迁导致材料表现出随着激光强度增加透过率降低的实验现象。利用非线性传播方程[43, 44]进行理论拟合（图3(b)），得到样品双光子吸收系数为～4.84×10^3 cm/GW，与过渡金属硫族化合物相当，具有很强的非线性吸收特性。当激光强度达到26.2 mJ/cm^{2}时进入第二阶段，样品透过率从40.2%突然下降到12.8%，同时反射率从6.6%急剧增加到12.0%，这是激光诱导VO_2从半导体相转变为金属相的结果。当VO_2处于半导体相时，样品对红外光具有较高的透过率；相变为金属相后，晶体结构的变化导致带隙消失，样品的吸收和反射作用增强，导致透过率显著降低。与温度诱导下VO_2透过率从42.2%下降到11.7%（图1(c)）相比，激光诱导材料相变几乎可以达到相同的效果，可以推断在

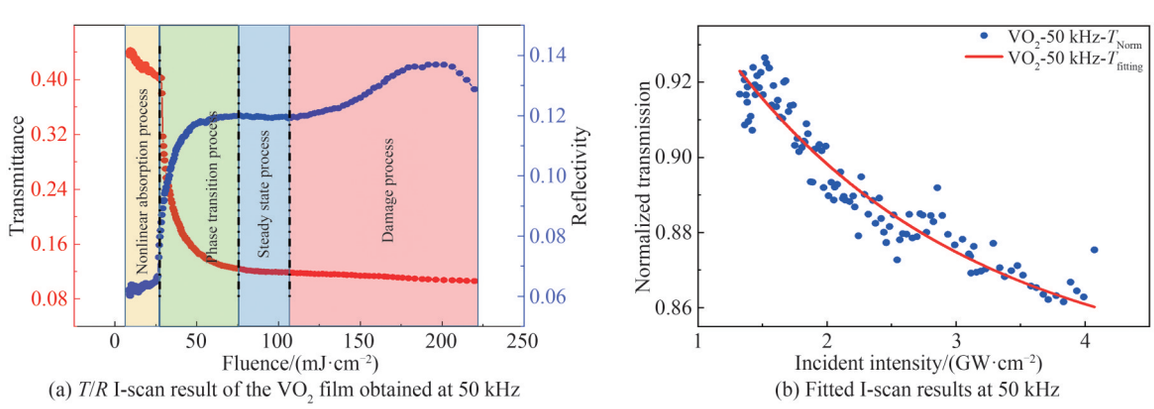


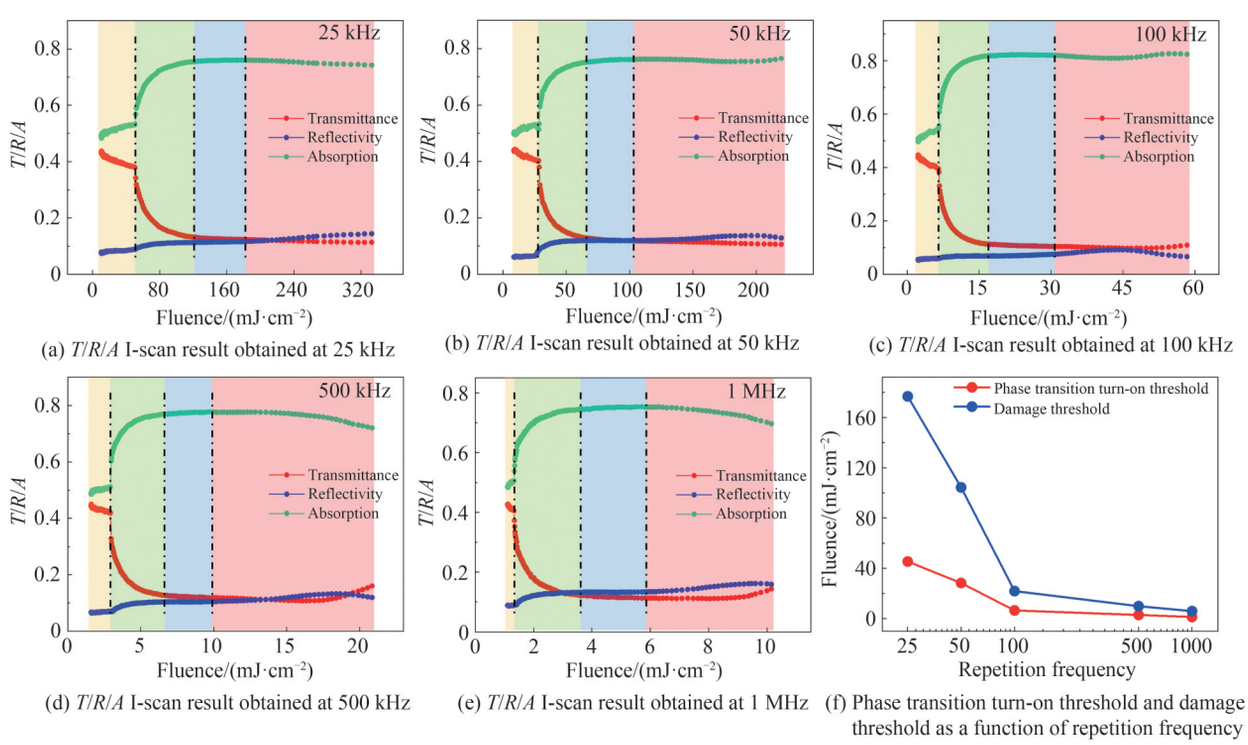
图3　激光诱导下二氧化钒光学特性

Fig. 3　Laser-induced optical properties of vanadium dioxide

激光作用下产生的光致相变是由温度场瞬时上升引起的热效应导致的。第三阶段为稳态过程，样品相变为金属相后透过率和反射率保持在相对平衡的状态，不再发生明显变化。当激光强度超过104.4 mJ/cm^{2}后，样品透过率开始下降，而反射率经过一个缓慢的上升后也开始下降，这是由于在激光作用下样品出现热损伤后导致反射率上升而在样品被穿透后反射率出现下降。随着激光强度的增加，VO_2经历了半导体相非线性吸收过程、半导体到金属相变过程、金属相稳态过程以及损伤过程，不同阶段导致样品透过率和反射率变化的机制不同，双光子吸收、激光诱导相变和激光热损伤都可以引起VO_2光学性质的改变。

2.2 不同重频下二氧化钒的光响应

为进一步分析VO_2在激光诱导下光学性质的变化过程，特别是激光热效应相变机理，测试了样品在不同激光重复频率下透射率(T)、反射率(R)随激光强度的变化关系，并利用公式$A=1-R-T$计算得到了样品吸收率(A)。如图4(a)～(e)，所有激光重频下的实验结果均表现为如图3(a)所示的四个阶段。在第一个非线性吸收过程，样品反射率变化不明显，非线性吸收的增强导致透过率略有下降。样品在第二个过程——相变过程中，光学性质变化最为显著，由半导体相转变为金属相后吸收明显增强。定义样品开始发生相变时的激光强度为相变开启阈值，如图4(f)，随着激光重复频率从25 kHz增大到1 MHz，诱导相变所需激光强度在经历一个迅速下降后几乎保持不变，开启阈值从45.4 mJ/cm^{2}减小到1.3 mJ/cm^2。稳态过程样品透过率、反射率和吸收率分别基本保持在11.5%、10.4%和78.1%，属于样品达到金属相后的固有性质，与激光重复频率无关。材料损伤过程随激光重复频率的增加越来越明显，损伤阈值从176.8 mJ/cm^{2}下降到5.9 mJ/cm^2(如图4(f))，激光热积累程度增加导致其损伤效果更严重，对样品造成的结构性破坏和击穿效果导致其吸收率的不规则变化，与相变开启阈值类似，在小于100 kHz激光重频时损伤阈值下降最明显。在激光作用下VO_2经历了半导体相、半导体-金属相过渡、金属相的过程，随着激光重复频率的增加，半导体相和金属相的透过率、反射率和吸收率等光学性质没有明显变化，但其相变开启阈值和损伤阈值明显下降，这是由于高重频激光作用下热效应的积累导致样品更容易发生相变和损伤。



(a) $T/R/A$ I-scan result obtained at 25 kHz (b) $T/R/A$ I-scan result obtained at 50 kHz (c) $T/R/A$ I-scan result obtained at 100 kHz

(d) $T/R/A$ I-scan result obtained at 500 kHz (e) $T/R/A$ I-scan result obtained at 1 MHz (f) Phase transition turn-on threshold and damage threshold as a function of repetition frequency

图4 不同重频激光诱导二氧化钒光学响应

Fig. 4 Variable frequency laser-induced vanadium dioxide optical response

3 结论

利用磁控溅射技术制备了VO_2薄膜，采用透/反射强度扫描实验装置研究了飞秒激光诱导下VO_2薄膜

的光响应。测量了1 036 nm波长下VO_2薄膜透过率随温度变化,验证了样品在68 ℃下经历半导体-金属相变,并具有明显的热滞回线。在此基础上,采用1 036 nm飞秒激光研究了VO_2薄膜光学性质随激光强度的变化关系,样品经历了非线性吸收过程、相变过程、稳态过程和损伤过程,非线性吸收过程归因于半导体相双光子吸收效应,样品在半导体-金属相变过程中由于强吸收导致透过率急剧下降。通过改变激光重频进一步证实了激光诱导相变是由于热积累导致的,随着激光重复频率的增加,由于激光热效应增加VO_2相变开启阈值和损伤阈值明显降低。系统分析VO_2在飞秒激光诱导下光学性质的变化及机制,将有利于该材料在光学领域的进一步发展。

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Femtosecond Laser Induced Optical Property Transition of Vanadium Dioxide (Invited)

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Abstract: Semiconductor-metal phase transition in metal oxides have attracted much attention due to their

scientific significance in condensed matter physics and their possibilities in a variety of applications. During the last half century, experimental and theoretical studies on phase transition mechanism have been discussed. Vanadium dioxide (VO_2) has attracted much attention due to its phase transition properties at room temperature. The VO_2 phase transition can be triggered by a variety of excitations, such as thermal, electrical, optical, magnetic field, and strain, and because the phase transition process is reversible and its optical properties change significantly, it is widely used in optical switches, smart windows, optical storage, and laser protection. With the rapid development of femtosecond laser technology, more and more researchers are involved in the study of laser-material interactions. The control of VO_2 phase transition on ultrafast time scale using optical means will benefit its potential applications in memory devices, ultrafast optical switches and bistable optoelectronic devices.

Firstly, we briefly introduce the basic properties of VO_2. The material undergoes a phase transition at room temperature (~68°C), which is reversible and non-destructive. Stimulated by external conditions, VO_2 transforms from a monoclinic semiconducting phase ($P2_1/c$) to a tetragonal rutile phase ($P4_2/mnm$) with a distortion of the lattice structure, accompanied by a change in electrical resistance of about four orders of magnitude and a consequent change in its optical properties. A common method for inducing semiconductor-metal phase transition is thermal triggering. Below the phase transition temperature, VO_2 is a semiconducting phase with a high transmittance, and when the temperature is heated above 68°C, VO_2 changes into a metallic phase with abrupt changes in its optical properties such as refractive index, transmittance, and reflectance. The phase transition can also be triggered on sub-picosecond time scales under femtosecond laser induction. Due to the extremely high response rate and significant optical property changes of laser-induced phase transition, it is important to study the laser-induced phase transition process, which will help to expand its applications in optical devices and systems.

Secondly, we prepared VO_2 film using magnetron sputtering, a kind of physical vapor phase deposition which is widely used for the synthesis of VO_2 thin films due to high deposition rate, uniform film formation, high reproducibility and suitable for large area preparation. The Atomic Force Microscope (AFM) image clearly shows the surface morphology of the sample, which is found to be uniform with a high flatness, and the thickness of the sample is ~195.5 nm. The XRD pattern shows a distinct diffraction peak at $2\theta = 40°$, corresponding to the (001) crystal plane, indicating that the sample is a well crystallized pure phase VO_2 (M). A typical thermogenic echo line is observed in the temperature-dependent transmittance curve, with the most pronounced change in transmittance near the phase change temperature, which drops sharply from ~42.1% to ~11.6%. The sample recovery temperature is at ~53 ℃ with an average hysteresis of ~15 ℃.

Thirdly, the optical response of VO_2 film under femtosecond laser induction was measured using a home-built transmission and reflection I-scan experimental setup. As the incident laser intensity increases, the sample changes of transmittance and reflectance show four different stages: nonlinear absorption process, phase transition process, steady state process and damage process. At lower laser intensities (less than ~26.2 mJ/cm^2), the VO_2 film maintains a high transmittance, showing a slight decrease from 43.9% to 40.3% with increasing laser intensity, while the reflectance remains essentially constant at ~6.3%, indicating that the sample does not undergo a phase change and remains in the semiconducting phase. This change is mainly attributed to the two-photon absorption process of the VO_2 semiconductor. When the laser intensity reaches ~26.2 mJ/cm^2, the sample transmittance suddenly decreases from ~40.2% to ~12.8%, while the reflectance sharply increases from ~6.6% to ~12.0%, which is the result of the laser-induced phase transition of VO_2 from the semiconducting phase to the metal phase. Compared with the temperature-induced transmittance change in VO_2, the same effect can be achieved by laser-induced, and it can be inferred that the phase change induced under the laser action is caused by the laser thermal effect. The steady state process is that the transmittance and reflectance remain in relative equilibrium after the sample phase changes to the metallic phase without significant change. When the laser intensity rises above ~104.4 mJ/cm^2, the transmittance of the sample starts to decrease, and the reflectance also starts to decrease after a slow increase, which is due to the thermal damage of the sample under the laser action. In order to further analyze the change process of optical properties of VO_2, especially the phase change mechanism of laser thermal effect, the transmittance (T) and reflectance (R) as a function of laser intensity are measured at different laser repetition frequencies, and calculated the sample absorbance (A) using the equation $A = 1-R-T$. The experimental results at all laser repetition frequencies show the four stages of laser-induced

VO_2. With the increase of the repetition frequency, the laser-induced phase transition turn-on threshold decreases from ~45.4 mJ/cm^2 to ~1.3 mJ/cm^2 and the damage threshold decreases from ~176.8 mJ/cm^2 to ~5.9 mJ/cm^2. The laser thermal effect is enhanced and the thermal accumulation of the sample increases due to the increase of the laser repetition frequency, leading to more susceptible to phase transition and damage.

Finally, a brief summary of the work is given, and we expect that this study will have a contribution to the further development of this material in the field of optics.

Key words: Vanadium dioxide; Femtosecond laser induction; Semiconductor-metal phase transition; Nonlinear optics; T/R I-scan

OCIS Codes: 140.7090; 160.4330; 190.4400; 190.4870; 250.4390

Foundation item: National Natural Science Foundation of China (No.61975221)