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10.6 μm Infrared light photoinduced insulator-to-metal transition in vanadium dioxide

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HIGHLIGHTS

- 10.6 μm Infrared can make VO_2 come to pass photo induced phase transition.
- We test the characteristic of vanadium dioxide when irradiating by CO_2 laser.
- We test the transmittance of 632.8 nm infrared light and transmittance of VO_2.

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ABSTRACT

Vanadium dioxide has excellent phase transition characteristic. Before or after phase transition, its optical, electrical, magnetic characteristic hangs hugely. It has a wide application prospect in many areas. Now, the light which can make vanadium dioxide come to pass photoinduced phase transition range from soft X-ray to medium infrared light (6.9 μm, 180 meV). However, whether 10.6 μm (117 meV) long wave infrared light can make vanadium dioxide generate photoinduced phase transition has been not studied. In this paper, we researched the response characteristic of vanadium dioxide excited by 10.6 μm infrared light. We prepared the vanadium dioxide and test the changes of vanadium dioxide thin film's transmittance to 632.8 nm infrared light when the thin film is irradiate by CO_2 laser. We also test the resistivity of vanadium dioxide. Excluding the effect of thermal induced phase transition, we find that the transmittance of vanadium dioxide thin film to 632.8 nm light and resistivity both changes when irradiating by 10.6 μm laser. This indicates that 10.6 μm infrared light can make the vanadium dioxide come to pass photoinduced phase transition. The finding makes vanadium has a potential application in recording the long-wave infrared hologram and making infrared detector with high resolution.

1. Introduction

Vanadium dioxide is a thermal-induced material. The change in the crystal structure of the vanadium dioxide before and after phase transition leads a major variety of its optical, electrical, magnetic characteristic. Besides, the phase transition time is in ns grade. All the reasons above make vanadium dioxide become an excellent functional material and have a wide application prospect. The examples are as follows: (1) Smart windows. (2) Laser protection. With the process of metal–insulator transition, especially the mutation of optical characteristic in infrared band, it can be taken as the laser protection material of the wave length from 3 to 5 μm and 8 to 12 μm [1]. (3) Infrared up-conversion material, such as micro-bolometer and thermal resistor. As transition metal oxide, its temperature coefficient of resistance is large, so they are the preferred thermal resistor. Vanadium dioxide is one of the good thermal resistor materials [2]. (4) Optical switch. At the phase transition point, the change of metal to insulator phase will occur and so, the transmittance and reflectivity of infrared light will change suddenly. This makes vanadium dioxide become good optical switch material [3]. (5) Variable mirror [4]. (6) Optical modulator. Vanadium dioxide thin film will generate a reversible phase transition between metal and insulator at about 68 °C. When we set the film at a temperature around 68 °C, we can make its optical contrast change with the temperature. This is the working theory of optical modulator.

In 1959, Morin first found the phase transition phenomenon of vanadium dioxide from insulator to metal. At the phase transition point, the conductivity, transmissivity, refractivity, susceptibility and specific heat will generate a reversible sudden change [5].

Since Morin discovered phase transition properties of vanadium oxide materials, for a long time, the research of vanadium oxide materials have been focused on the preparation of vanadium oxide

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thin films, which have a high resistance temperature coefficient, and suitable resistivity, mainly for heat sensitive materials of uncooled infrared detectors. The widely-used vanadium oxide uncooled thermal imaging systems are included in these typical results.

At the beginning of this century, the phenomenon of phase transition properties of vanadium oxide materials has been attentioned by scientists, and one of the important researches is photoninduced phase transition of vanadium oxide. In 2001, Cavalleri, in Oxford University, with his leadership team published a paper, which introduced the achievements about structural dynamics in the process, led by femtosecond lasers, of the phase transition of vanadium dioxide [6]. The research finding shows that: the phase transition effect of vanadium dioxide observed in the experiment is not due to thermodynamic reason. In 2004, Cavalleri and his team reported using soft X-ray photoninduced achieved metal–insulator phase transition of vanadium dioxide thin films [7]. In 2005, Cavalleri and his team reported using 800 nm laser to induce vanadium of dioxide and achieved metal–insulator phase transition [8]. Since then, the test and analysis of the optical and electrical properties in the process of phase transition of vanadium dioxide materials have been focused by more and more researches. In 2008, Ashrit, from Canada, leaded his team and published papers in <OC> and <APL> [9,10], which was the research on the phase change of metal–insulator induced by photons of vanadioxide. Iconic achievements included two aspects: (1) Ashrit induced vanadium dioxide films of different thickness (100 nm–300 nm) with Nd:YVO4 laser, which energy is 5 W, and the wavelength is 532 nm. The result showed that vanadium dioxide films with different thicknesses can be observed apparent metal–insulator phase transition effects. (2) By testing the permeability of vanadium dioxide film, Ashrit found the dynamic range of its transmittance in the near infrared band reached 68 db, much higher than the previous 42 db. However, the experimental results from Ashrit still lack adequate theoretical foundation. Authors themselves also admitted frankly that it needed further study. In 2008, Cavalleri and his team, showed that: although the band gap of the vanadium dioxide material is 670 meV, the threshold needed by the photoninduced phase transition effects of single-crystal and polycrystalline vanadium dioxide film had significant differences. For the single-crystal vanadium dioxide, only when the photon energy is greater than 670 meV, it can achieve photoninduced phase transition effect, but for the thin films of polycrystalline vanadium dioxide, can achieve photoninduced phase transition effect as long as the photon energy is larger than 180 meV [11]. Although a complete theoretical explanation is not given, but by experimental tests, Cavalleri and his team have confirmed firstly that photoninduced of vanadium dioxide thin films can be achieved by mid-infrared.

In 2011, Davila pointed out that increasing the wavelength gradually, which could cause photoinduced phase transition in vanadium dioxide, would be a development direction in the future [12]. In 2012, Cavalleri's team continued to expand the infrared wavelengths in $Pr_{0.7}Ca_{0.3}MnO_3$ material [13], which caused photoinduced phase transition, and published the latest research results. With the use of 17 μm infrared light around photon energy, they successfully made $Pr_{0.7}Ca_{0.3}MnO_3$ material generate photoinduced phase transition, and tested the phase transition performance by the use of the 800 nm near-infrared light.

Considering the wavelength of the Co_2 laser, can 10.6 um infrared light make the vanadium dioxide generate phase transition? What is the phase transition characteristic? To the best of our knowledge, there is yet no research about them in vanadium dioxide material. Therefore, we will carry on the preparation of vanadium dioxide thin films, and acquire the vanadium dioxide thin film properties through exciting the vanadium dioxide thin film by 10.6 μm laser.

The paper is arranged as followings. Section 2 is the preparation of vanadium dioxide thin film. The phase transition characteristics of vanadium dioxide are tested in Section 3. Section 4 concludes the paper.

2. Preparation of vanadium dioxide thin film

2.1. Experimental preparation

We prepare vanadium dioxide thin films by RF magnetron sputtering. The power frequency of RF sputtering is 13.56 MHz, and the adjustable output power is 0–500 W. The water-cooled metal machine target whose diameter is 60 mm and purity is 99.7% is chosen as the sputtering target. The sputtering gas is high purity hydrogen gas (99.999%), and the reactant gas is high purity oxygen gas (99.99%). The flow of the gas is dynamic controlled and monitored through the mass flow meter. The mechanical pump is taken as forepump, and molecular pump as the secondary pump which pumps the base vacuum under 10^{-5} Pa. Then turn on the heating device, the heating process is controlled by thermostat. The substrate temperature is measured by nickel–copper–nickel aluminum thermocouple. After heating to the setting temperature (500 °C), we pass into oxygen and Ar, the flow of which is 0.1 sccm and 38 sseem, separately. In the preparation process, the other working parameters are: the sputtering power is 120 W, pressure plate is 750 V, plate current is 200 mA, and self-bias is 200 V.

2.2. The growth of thin films

The growth of films is a phase transition process from gaseous phase to adsorbed phase, and then to solid phase, which can be roughly divided into four stages: nucleation, combination, channel film, and continuous films.

In the process of film growth, the substrate temperature T_s is an important factor affecting the organizational structure of the films. The current research indicates that the organizational structure of films change with the substrate temperature T_s relative to the melting point T_m of films, and it can be divided into four zones [12]:

Zone I: $T_s < 0.15T_m$. Since T_s is low, the additional energy cannot be obtained by the adsorption of atoms from the substrate to improve the surface mobility, which leads to the extreme weakness of surface diffusion. Most atoms can only gather together with other incident atoms near the original position of adsorption into a nucleus. However, after the formation of stable crystal nucleation, there is still not high enough energy to overcome the grain boundary barrier and combine with adjacent crystal nucleus. Therefore, the grains of crystal films growing in the zone I have a small size (much smaller than the film thickness), which is within several to dozens of nanometers. The voids in the grain boundary have a larger density, and the film texture is loose.

Zone T: $0.15T_m < T_s < 0.3T_m$, a transition area between zone I and zone II. In this area, the surface diffusion of adsorbing atoms is improved, the density of gap is reduced greatly, and the grain between grain crystals becomes apparent. With the increase of T_s, part of the grain crystals can overcome grain boundary barrier, and combine together to form a larger (but still less than the film thickness) grain, so that the proportion of large size grains increases gradually.

Zone II: $0.3T_m < T_s < 0.5T_m$. The surface diffusion and grain boundary migration are remarkable. Crystal nucleus combines

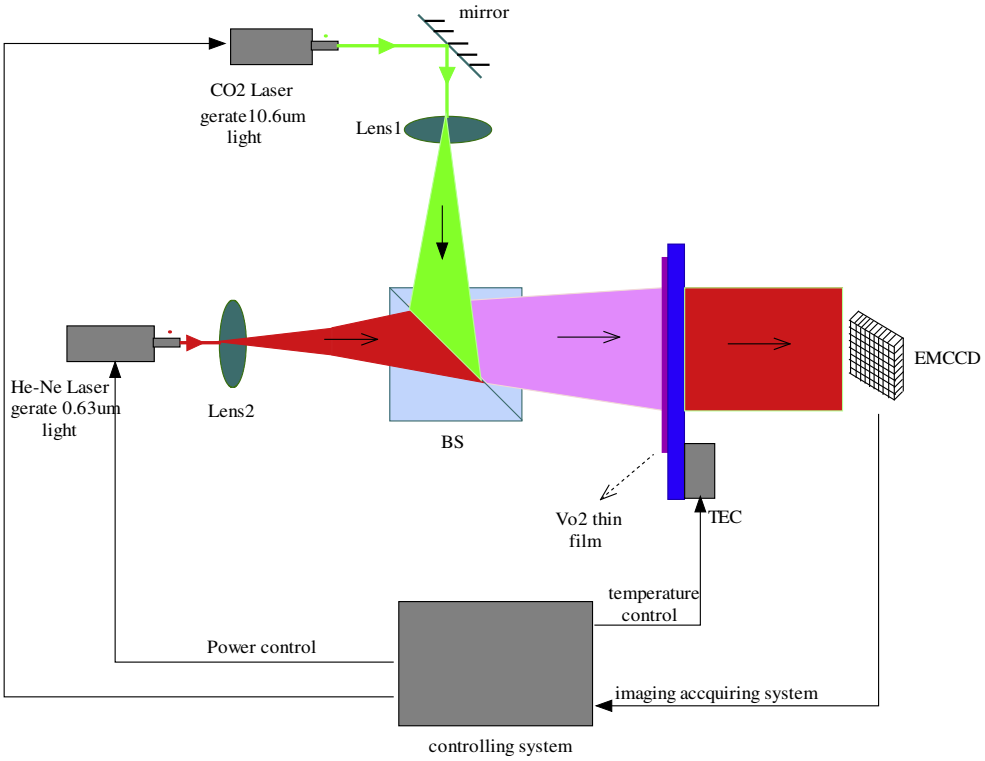

Fig. 1. Optical parameter test system of vanadium dioxide when excited by 10.6 μm laser. Bs: beam. spliter. EMCCD:L3C216 produced by E2 V company of England.

together into columnar grain with compact arrangement whose length equals to film thickness. With the increase of T_s, the diameter of columnar grain increases. The structure of crystal films growing in zone II is very dense, which achieves the density of block materials.

Zone III: $T_s > 0.5T_m$. Bulk Diffusion and recrystallization become significant, and grain boundaries are less. The grain size is very large (diameter can be more than film thickness), with the characteristics of columnar or equiaxed growth.

When preparing thin films by sputtering method, the pressure of working gas (such as Ar) is another factor which affects the tissue structure of films.

In general, working gas mainly has an obvious influence on the tissue structure of films in zone I and zone T [12]. Because T_s of these two zones is low, molecules of working gas are easy to be absorbed by substrate surface. This will limit surface migration of films' absorption of atoms, and shorten the diffusion length. The higher the working gas pressure is, the weaker the quality of surface diffusion of films absorbing atoms is. This eventually leads to the bigger density of gap between grain boundaries, which makes zone I broadened, zone T narrowed.

However, in zone II and zone III of high T_s, because molecules of working gas are easy to achieve desorption from the substrate surface, tissue structure of films are influenced less by Ar.

2.3. Annealing treatment

Annealing treatment plays a key role to improve the thermal stability of the film. It is important that during the preparation of the film it can be subjected to the subsequent series of hest treatment while maintaining the basic performance of the same. Film surface growth at low temperatures is relatively flat. While, during the annealing process, due to thermal fluctuations of the emergence, the film surface is no longer flat and the local area will bend. Thermal fluctuations will cause the atoms depart from the original location or surface diffusion. The strength of these two cases depends on the annealing temperature. When it is above the critical temperature, the surface morphology may change to rough and reach another more stable thermodynamic state.

In experiment, the crystalline vanadium dioxide film (substrate temperature is 250 °C) anneals directly in vacuum coating machines. The annealing vacuum degree is high vacuum (10^{-4} Pa) and low vacuum (0.2 Pa), the annealing temperature is in the range from 35 °C to 560 °C, holding time are 5 h, heating rate and cooling rate are at 8 °C/min and 10 °C/min separately. The temperature fluctuation is controlled within ±1 °C. Through the experiments above, we prepared a VO_2 thin film with thickness of 15 nm.

3. Test of phase transition characteristic

We adopt the following test method to test optical properties of vanadium dioxide thin film.

In Fig. 1, Co_2 laser emits 10.6 μm infrared laser which irradiates onto the BS after the reflection mirror and the diffusion Lens1, then irradiates to the vanadium dioxide thin film by BS. The infrared light will make vanadium dioxide thin film generate phase transition. Since the 10.6 μm light cannot penetrate vanadium dioxide thin film, the primary role of the light is to change the optical properties of vanadium dioxide thin film. The 632.8 nm laser generated by He–Ne laser irradiates to the BS after it diffused by Lens2, finally it is projected onto vanadium dioxide thin film. Light energy transmitted through the vanadium dioxide film can reflect the phase transition characteristic of vanadium dioxide thin film by EMCCD. EMCCD has high sensitivity. In the test process, we increase EMCCD gain and exposure time, and make EMCCD exposure frequency equal to He–Ne laser operating frequency. The temperature of the vanadium dioxide thin film is controlled at 30 °C by TEC. Under these conditions,

we test the output response of EMCCD at different transmit power of He–Ne laser. The test results are showed in Table 1. The test data are plotted in Fig. 2.

The data can be seen in Table 1. When power of CO_2 laser is switched off, 632.8 nm laser cannot pass through vanadium dioxide thin film. However, when the power of CO_2 laser ranges from 2 to 4 W, EMCCD can receive 632.8 nm laser, and the transmittance of vanadium dioxide thin film (A/B) does not change significantly. Its change interval of the data is 1.230–1.240. This data shows that, with He–Ne laser power increasing, the energy of the 632.8 nm laser which penetrates vanadium dioxide thin film increases gradually. This indicates that the 10.6 μm laser makes vanadium dioxide thin film phase transition. When CO_2 laser power increases from 2 w to 3 w, even up to 4 w, the transmittance of the vanadium dioxide thin film does not change significantly (minor changes are brought by the EMCCD noise). This shows that, although the energy of the CO_2 laser becomes larger and larger, phase transition properties of vanadium dioxide films does not change. This phenomenon indicates that the cause of the change of vanadium dioxide is photoinduced phase transition, rather than thermal induced phase transition. When the power of CO_2 laser increases to 5 W, the transmittance of the 632.8 nm laser is increasing rapidly, reaching between 1.25–1.35, which indicates that vanadium dioxide thin film generates thermal induced phase transition. In this case, the parameters of optical properties are not completely determined by the photon energy of the CO_2 laser. Fig. 2 shows a very clear and similar analysis.

In addition, in order to avoid 632.8 nm light impacting on the phase transition of the vanadium dioxide, we test the resistivity of vanadium dioxide under the excitation of the 10.6 μm laser to determine the long wave infrared light impact on vanadium dioxide phase transition. Fig. 3 shows the resistivity curve of the vanadium dioxide thin film with10.6 μm laser power.

Table 1
Contrast of power of co_2 laser and output response of EMCCD.

Power of Co_2 laser (W)	(A) Power of He–Ne laser (mW)	(B) Output response of EMCCD (V)	A/B	Power of He–Ne laser (mW)	(A) Power of He–Ne laser (mW)	(B) Output response of EMCCD (V)	A/B
0	1	0		0	2.0	0	
	1.2				2.2		
	1.4				2.4		
	1.6				2.6		
	1.8				2.8		
2	1	0.81	1.235	4	1	0.80	1.250
	1.2	0.97	1.237		1.2	0.97	1.237
	1.4	1.13	1.239		1.4	1.14	1.228
	1.6	1.29	1.240		1.6	1.30	1.231
	1.8	1.46	1.233		1.8	1.45	1.241
	2.0	1.62	1.235		2.0	1.63	1.227
	2.2	1.78	1.236		2.2	1.79	1.229
	2.4	1.95	1.231		2.4	1.96	1.224
	2.6	2.11	1.232		2.6	2.11	1.232
	2.8	2.26	1.239		2.8	2.26	1.239
	3.0	2.43	1.235		3.0	2.42	1.240
3	1	0.81	1.235	5	1	0.77	1.299
	1.2	0.97	1.237		1.2	0.92	1.304
	1.4	1.14	1.228		1.4	1.07	1.308
	1.6	1.30	1.231		1.6	1.22	1.311
	1.8	1.46	1.233		1.8	1.37	1.314
	2.0	1.62	1.235		2.0	1.52	1.316
	2.2	1.79	1.229		2.2	1.67	1.317
	2.4	1.94	1.237		2.4	1.82	1.319
	2.6	2.10	1.238		2.6	1.97	1.320
	2.8	2.27	1.233		2.8	2.12	1.321
	3.0	2.44	1.230		3.0	2.27	1.322

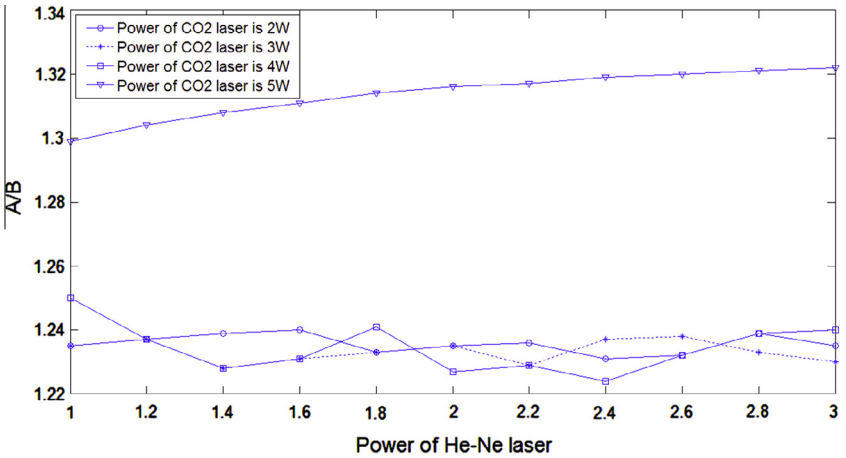

Fig. 2. Phase transition characteristic of VO_2 at different laser power.

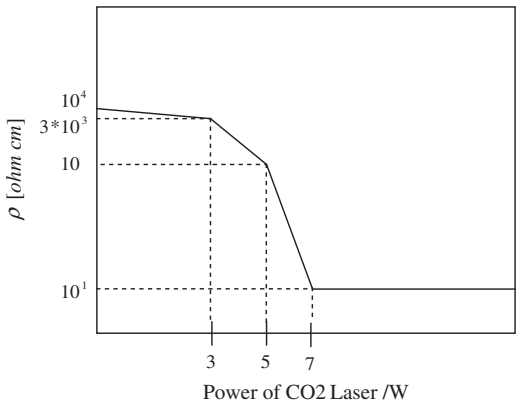

Fig. 3. Relation of resistivity and power of CO_2 laser.

It can be seen from Fig. 3, when the laser power is less than 3 W, the resistivity of the vanadium dioxide thin film does not change significantly, but when the power change from 3 W to 5 W, the resistivity of vanadium dioxide thin film decreases rapidly. When the power of CO_2 laser changes from 5 W to 7 W, the resistance rate almost plummets down. The figure shows when the CO_2 laser power increases gradually, the resistance has two obvious mutations. This suggests that the VO_2 thin film under the stimulus of CO_2 laser generate phase transition. However, in the 3–5 W power, photoinduced phase transition occurs. And when the CO_2 laser power increases, the temperature of the VO_2 thin film rises, and more obvious thermal induced phase transition occurs. This result is consistent with the experimental results of the change in transmittance of 632.8 nm light.

4. Conclusion and outlook

In conclusion, in this paper, we prepared a vanadium dioxide thin film and demonstrate that 10.6 μm infrared light can make the photoinduced phase transition in the vanadium dioxide thin film by two experiments. The first experiment, we first use of Co_2 laser to irradiate VO_2 thin film, and use EMCCD to test the change of the vanadium dioxide thin film in the 630 nm light transmittance. It is found that when CO_2 laser power is between 2 W and 4 W, the transmittance of 630 nm laser does not change significantly. And when the laser power increases to 5 W, there has been a marked change on the transmittance of 630 nm laser. This suggests that the vanadium dioxide thin film under the excitation of CO_2 laser has experienced the process from photoinduced phase transition to thermal induced phase transition. In the second experiment, we also adjust the CO_2 laser power, and test the changes of the resistivity of vanadium dioxide thin film. The esistivity of vanadium dioxide thin film has experienced two same mutations, which are consistent with the results of the first experiment. The experimental results show that 10.6 μm long wave infrared light can make photoinduced phase transition in the vanadium dioxide thin film. This finding can expand the application areas of vanadium dioxide material. In the long wave infrared holographic records and long wave infrared detector material there are potential applications. Of course, this paper does not analyze the conditions of vanadium dioxide thin film photo phase transition by 10.6 μm laser, the range of the change of optical properties and phase change theory, this will be studied in the near future.

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