Damage characteristics of VO$_2$ films under nanosecond/picosecond laser

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Abstract. Vanadium dioxide films were prepared by magnetron sputtering method. An experimental apparatus for laser damaging VO$_2$ thin film was set up. Nanosecond laser and picosecond lasers were used to irradiate the thin film. The damage morphology of the thin film under these two kinds of laser was observed by metallographic microscope. Under the action of nanosecond laser, the damage of thin film is mainly thermal damage, which is mainly determined by the energy contained in the laser pulse itself, and the required damage threshold is relatively higher. The zero probability damage threshold of monopulse irradiate the film is about 0.13 J/cm$^2$. Under femtosecond laser, the damage of thin film is caused by multi-photon ionization and avalanche ionization, and the damage threshold is relatively lower. The zero probability damage threshold of monopulse irradiate the film is about 10.2 m J/cm$^2$.

1. Introduction
The vanadium oxide has many valence states. It will undergo a phase transition at a certain temperature and show different optical and electrical properties. In 1959, Miron, a scientist at bell LABS, first discovered that vanadium oxides have the characteristics of semiconductor-metal phase transition[1]. Among many valence states of vanadium oxide, the phase transition temperature of VO$_2$ is close to room temperature, which is about 68 ℃. Near the phase transition point, the gap width of VO$_2$ will change, and the phase transition from insulator to metal will occur. The physical parameters of the material (such as refractive index, infrared transmittance, resistivity, etc.) will change, and the macroscopic manifestation is the abrupt change of optical and electrical properties before and after phase transition[2][3].

In recent years, new features of vanadium dioxide have been discovered continuously, making it a research hotspot[4][5]. Such properties make vanadium dioxide have many potential applications in intelligent Windows[6], laser protection[7][8], solar energy, camouflage[9] and other aspects.

In infrared band, vanadium dioxide thin film has quite a high transmittance change before and after phase transition, which makes it have good application prospect in laser protection field. In this paper,
vanadium oxide thin films were prepared with sapphire as the substrate, and the damage characteristics of vanadium oxide thin films under nanosecond laser and picosecond laser were studied.

2. damage experiment of Laser Irradiating VO₂ thin film

2.1 experimental equipment

Experimental device of laser irradiating damage vanadium oxide thin film is shown in FIG. 1. The laser emits a certain amount of energy, which is attenuated by the rotating wave plate and adjusted to the required energy value. Then the laser is focused by lens and irradiated on the vanadium dioxide thin film sample. The vanadium dioxide thin film samples are placed on the adjustable sample rack. The height and left and right positions of the sample rack are adjusted to make the laser shine on different points. The damage characteristics of these irradiated points under laser irradiation were observed. At the same time, a beam splitting mirror is used to output a part of the laser energy to an energy meter.

The thin film used in the experiment was prepared by magnetron sputtering method, and the base material was single crystal alpha-Al₂O₃, which's diameter was 2 inch, thickness of Al₂O₃ was 200nm and VO₂ film thickness was 400nm.

![FIG. 1 schematic diagram of laser damaging VO₂ thin film test](image)

| Table 1 laser parameters in damage test |
|----------------------------------------|
| **Nanosecond laser parameters**        | **Femtosecond laser parameters**   |
| Wave length                            | 1064 nm                           | Wave length                           | 850nm                      |
| Pulse repetition rate                  | 1Hz                               | Pulse repetition rate                 | 10Hz                      |
| Pulse width                            | 10ns                              | Pulse width                            | 50fs                      |

3. Experimental results

3.1 damage threshold analysis

The laser irradiation point was directly observed by metallographic microscope. By observing the damage of each grade of energy density to the irradiation point on the thin film, the damage probability of the thin film under different pulse energy density was obtained.

After multi-point test, it was found that the 1-on-1 zero-probability damage threshold of VO₂ thin film under nanosecond laser was about 0.13J /cm². The zero probability damage threshold under femtosecond laser 1-on-1 irradiation is about 10.2m J/cm². The damage threshold under femtosecond laser is much lower than that under nanosecond laser. The damage threshold is related to the pulse width of the irradiation laser, and the narrower the pulse width is, the lower the damage threshold of the thin film is. 


3.2 damage morphology and evolution law analysis

3.2.1 nanosecond laser damage morphology and evolution law

The nanosecond laser is used to irradiate vanadium oxide thin film, adjust the power of the incident laser, irradiate on different points of the film, observe the damage rule of each point.

It was magnified 200 times by a metallographic microscope for observation. The damage morphology is shown in figure 2.

![Damage Morphologies at Different Laser Power Densities](image)

FIG. 2 micromorphologies of VO$_2$ film damage at different nanosecond laser power densities

It can be seen from figure 2 that the damage area of the thin film gradually expands with the increase of incident laser energy density. This is because the pulse width of nanosecond laser is relatively wide, and the main damage of thin film is thermal damage, which is mainly determined by the energy contained in the laser pulse itself. When the pulse width of laser pulse is nanosecond, the relationship between pulse energy and laser energy density is:

$$W_p = p_p \times \tau_p \times S_p$$

In the formula, $W_p$ is the laser pulse energy film received, $p_p$ is incident laser energy density, $\tau_p$ and $S_p$ are the pulse width and irradiated area respectively. When the spot radius and pulse width of the laser are the same, the higher the laser energy density is, the higher the pulse energy received by the film will be, and the larger the damage area will be under the effect of thermal diffusion.

By observing the damage morphologies at different energies, it can be found that: the damage morphologies of the thin films are all arc-shaped and wavy. With the increase of laser energy density, the damage morphologies gradually expand from inside to outside, and the outer arc length is smaller than the inner one.

This kind of arc ripple damage is caused by the melting of VO$_2$ film. When the incident laser energy reaches the damage threshold of the film, the film melts to form a accumulation layer. With the enhancement of laser energy, heat transfer to the outside causes the melting of the outer VO$_2$ film, leaving a wavy burn and melt trace in its heat transfer direction.

Since the nanosecond pulses used are gaussian lasers, the central energy is greater than the outside, resulting in the melting shape of VO$_2$ thin film showing a narrow arc with a wide middle and narrow sides. With the transfer of heat from inside to outside, the damage arc length becomes shorter gradually. It can also be found that for the same film, each wave bends in the same direction at different laser energies. This is because the pulse of the nanosecond laser is wider than the carrier-lattice energy transfer relaxation time of ps magnitude in VO$_2$. At this time, the damage is mainly caused by the lattice heat effect, and the ripple direction is related to the lattice orientation of the thin film itself. For films which have same lattice orientation, the wavy bending direction is same.
When the nanosecond laser energy density continues to increase to 0.322 J/cm$^2$, the damage morphology is shown in figure 3.

![Damage morphology of VO$_2$ film under nanosecond laser of 0.322 J/cm$^2$](image)

(a) Magnified 200 times  
(b) Magnified 600 times

FIG. 3 damage morphology of VO$_2$ film under nanosecond laser of 0.322 J/cm$^2$

With the energy of the nanosecond pulses continued to increase, a dark pit about 20 microns deep appeared in the center of the spot. This is due to the excessive energy density of nanosecond laser pulse at this time, which causes the VO$_2$ film in the central region to be completely stripped and the laser continues to ablate Al$_2$O$_3$ substrate.[11] In FIG. 3b, the Al$_2$O$_3$ substrate exposed at the ablation center and the surrounding accumulation can be clearly seen. Many irregular polygonal squares in the accumulation also indicate that it has obvious melting and cooling traces.

3.2.2 damage characteristics of VO$_2$ films under picosecond laser

The femtosecond laser was used to irradiate vanadium oxide films, and the energy density of incident laser was adjusted to observe the effect of femtosecond laser energy density on the damage morphology of VO$_2$ films. With different power densities, damage morphologies were observed, as shown in FIG. 4.

![Damage morphology of VO2 films exposed by femtosecond laser](image)

(a) 20 mJ/cm$^2$  
(b) 40 mJ/cm$^2$

(c) 80 mJ/cm$^2$  
(d) 140 mJ/cm$^2$

FIG. 4 damage morphology of VO2 films exposed by femtosecond laser

To observe subtle morphology, The image of the damaged area is enlarged more, as shown in FIG. 5.
It can be seen from the experiments that the damage morphologies of VO$_2$ films under nanosecond laser and femtosecond laser are quite different. Compared with the two, there are the following characteristics: (1) Damage sizes, the maximum diameter of femtosecond laser damage is only 20 microns, which is because the overall energy of femtosecond laser used is much smaller than that of nanosecond laser, and only the laser irradiation area is damaged. (2) Damage morphology: the damage morphology of nanosecond laser is an outward-inward semi-ripple, while that of femtosecond laser is an outward-extending concentric ring. When femtosecond laser energy is low, the circle of damage morphology does not close, and the damage only occurs in the direction parallel to the laser polarization. With the increase of femtosecond laser energy, the concentric ring gradually closes, which basically conforms to the geometric morphology of gaussian beam. This indicates that the damage morphology induced by femtosecond laser is closely related to its light intensity or energy density.

### 3.2.3 Comparative analysis of femtosecond laser and nanosecond laser damage characteristics of VO$_2$ films

Femtosecond laser and nanosecond laser have different processes in the interaction between laser and vanadium dioxide film. When the incident laser is a nanosecond laser, its pulse is wider than the carrier-lattice energy transfer relaxation time (ps order) in VO$_2$, and most of the absorbed energy is used to increase the material temperature. At this time, the VO$_2$ film is a pure thermodynamic process, and the damage caused by nanosecond laser to the film is thermal damage, which requires a high damage threshold.

When femtosecond pulse laser is irradiated on VO$_2$ thin film, multi-photon ionization and avalanche ionization will occur, and the damage process is related to the increase of free electron density in VO$_2$ thin film. Under the irradiation of femtosecond laser, the electrons in VO$_2$ valence band are excited to the conduction band, and the free electron density is increased. When the free electron density in the system is greater than the critical value ($10^{21}$ cm$^{-3}$), a large number of covalent bonds in VO$_2$ are destroyed, resulting in weakened binding force in the lattice of vanadium dioxide. VO$_2$ lattice tends to be disordered, causing damage.

The process time is very short (<100fs), which is far less than the lattice thermal effect relaxation time, so the damage will occur before the lattice heating. This process is called cold ablation.

The change rate equation of the free electron density in the material under the action of femtosecond laser can be expressed as follows:

$$\frac{dN}{dt} = \alpha IN + \beta I^m - \frac{N}{\tau} - \Gamma \nabla^2 N$$

(2)

Where, $N$ is the electron density, $I$ is the pulse light intensity, $\alpha$ is a constant representing the avalanche process, $\beta$ is a constant representing the dissociation process of multiple photons, $\tau$ is the free electron density relaxation time, $\Gamma$ is the free electron diffusion coefficient, $m$ is the absorption coefficient of photons.

It can be seen from formula 2 that the change rate of free electron density dN/dt IN the material is mainly related to avalanche ionization process represented by $\alpha IN$ and multi-photon absorption process represented by beta $\beta I^m$, both of which are related to laser intensity $I$. 

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FIG. 5 details of damage morphology evolution of VO$_2$ films under femtosecond laser irradiation

(c)80 mJ/cm$^2$ (d)140 mJ/cm$^2$
Therefore, the mechanism of femtosecond laser thin film ablation will be different with the difference of laser intensity or laser energy density. It is pointed out that the avalanche ionization mechanism plays the leading role under the action of lower laser energy density, and the damage morphology is elliptic. At a higher laser energy density, multi-photon absorption and free electron diffusion dominate, and the ablation morphology is nearly circular [12].

4. Summary
Vanadium dioxide films were prepared by magnetron sputtering method. The damage morphology of the thin film was observed by nanosecond and picosecond laser irradiation. Under the action of nanosecond laser, the damage of thin film is mainly thermal damage, which is determined by the energy contained in the laser pulse itself. Under the action of femtosecond laser, the damage of thin film is caused by multi-photon ionization and avalanche ionization, and the required damage threshold is low.

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