Nonlinear optical properties of the vanadium dioxide films

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Abstract. In this work the properties of vanadium oxides films are investigated for optimizing their nonlinear optical coefficients. Vanadium oxides films are studied obtained by pyrolysis of vanadyl acetylacetonate. Experimental determination of parameters of films was carried out by measuring the dependencies of reflectivity and conductivity with temperature. The results show that the variation of the thickness of vanadium oxide films can significantly change their optical performance.

1. Introduction
Vanadium oxides belong to materials with thermoinduced semiconductor-metal phase transition (PTSM) [1]. When heated in the field of phase transition the semiconductor goes into metal state and then it changes its optical properties [2]. The phase transition in vanadium dioxide is a well-studied example where the process can occur in less than a picosecond, making it interesting for ultrafast optical switches [3]. Among the established work, ultrafast insulator-metal transition (IMT) has been the early focus using ultrafast optical pump-probe techniques [4-6].

In a number of works it was illustrated the using of vanadium dioxide for optical information recording and optical bistability scheme [1, 6]. It was realized the dynamic holography experiments in the visible range of the spectrum [1]. The change of optical constants of VO$_2$ is a much larger amount in the infrared range (IR) of the spectrum. Thus, this material is more convenient for using the lower recording radiation, including the wave continuous laser sources.

Nonlinear optical characteristics of this material depend from technological conditions for obtaining films. It was shown that the varying of technological conditions change the critical temperature and the width of the PTSM on the great values [1, 7].

In this work the capabilities of technological management by the parameters of vanadium oxides films are investigated for optimizing their nonlinear (IR) optical properties.

2. A model of the nonlinear optical material with phase transition
Undergoing PTSM the vanadium dioxide has quite great absorption, therefore nonlinear interaction of waves is effectively only in thin films, which naturally leads to a scheme using the surface dynamic holograms [8, 9]. In the latter case, a dynamic hologram is a grating of the amplitude reflectance (assuming that the optical surface characteristics can change under the influence of the incident radiation). Mechanisms of surface nonlinearity may be different, but all of them can be described using complex amplitude dependence of radiation reflectance $\rho$:

$$\rho(I) = \rho(I_0) + \beta \delta I(x, y),$$  \hspace{1cm} (1)
where $I_0$ is the average radiation intensity, $\beta = (d\varphi/dI)$ is the coefficient of the surface nonlinearity, $\delta I(x, y)$ is the space distribution of the recording intensity of radiation on the film surface.

For the thermoinduced phase transition the nonlinear coefficient is determined by the next expression:

$$\beta = (dR_F / dT) (dT / dI) / 2 R_F^{0.5},$$

where $T$ is the surface temperature, $R_F$ is the coefficient of Fresnel reflection, $R_0$ is the coefficient of Fresnel reflection in the middle of the PTSM.

The equation (2) shows that the value of the nonlinear coefficient is determined by the differential (jump) of reflectivity during the temperature changes in the SMPT field.

The coefficient of the surface nonlinearity is determined by change in the reflectivity and was calculated as:

$$\beta_T \approx (\Delta R_F / \Delta T_p)$$

where $\Delta R_F = (R^{M}_F - R^{S}_F)$. $R^{S}_F$ is the coefficient of Fresnel reflection for semiconductor phase, $R^{M}_F$ is the coefficient of Fresnel reflection for metal phase, $\Delta T_p$ is the PTSM width.

In simplest case (the thickness of the substrate and film are small enough) the temperature of the VO$_2$ film was defined from the solution of one-dimensional heat task:

$$(dT / dI) = L \chi^{-1} (1 - R_F)$$

where $L$ is the thickness of the substrate ($L >> d$, $d$ is the thickness of the VO$_2$ film), $\chi$ is the thermal conductivity of the substrate.

The final expression for coefficient of the surface nonlinearity is:

$$\beta = \beta_T L \chi^{-1} (1 - R_F) / 2 R_F^{0.5},$$

PTSM in the vanadium dioxides films usually is characterized by significantly width. It is generally assumed that the most likely reason for the coexistence of two phases at a given temperature is the presence of mechanical stress and in particular inhomogeneities in composition, which can pretty much change the local temperature of phase transition. The reason for this difference is that the hysteresis loop of VO$_2$ film consists of elementary hysteresis loops of individual crystallites that make up the film [2]. The position on the scale of temperatures and the width of the basic loops are different for different crystallites. It follows that the total width of the PTSM determined by basic widths of the corresponding crystallites loops and the distribution of basic loops on their widths.

The model assumes that each grain-film crystallite has one inherent basic thermal hysteresis loop and that basic loops of individual crystallites films are "vertical" for temperature. It follows that the total width of the SMPT in vanadium dioxide sample is determined by basic widths of crystallites loops corresponding to the maximum of the distribution of basic loops on their widths.

The critical temperature and hysteresis loops form has also been impacted by the presence of impurities in VO$_2$ and excess or lack of oxygen in the film. Deviation of the oxygen content in the film as in larger and smaller side leads to increased temperature interval.

3. Experimental results

Optical parameters are related to physical characteristics of the thin films samples. To establish this connection, it was investigated the dependence of reflectance $R_F$ (wavelength 10.6 μm) and resistance (in the planar geometry) of the samples from the temperature in the PTSM region.

The measurements were carried out for vanadium dioxides films with different thickness of the samples. The vanadium dioxides films obtained by pyrolysis of vanadyl acetylacetonate were explored.
The reflectance coefficient was measured for close to normal radiation angles. The heating was undertaken both laser radiation and independent manner. The change in the reflectivity of the vanadium dioxide films was experimentally measured with the infrared laser radiation (wavelength is 10.6 µm).

Figure 1 shows the change in the reflectivity at PTSM versus VO$_2$ film thickness.

![Figure 1](image1.png)

**Figure 1.** The coefficient $\Delta R_F$ versus the thickness of the vanadium dioxide film.

Figure 2 shows the PTSM width versus VO$_2$ film thickness. The coefficient of the nonlinearity $\beta_T$ was calculated using the experimental dates (figures 1 and 2) and is shown in the figure 3.

As the result it was established that the surface nonlinearity reaches the maximum in thick samples of vanadium dioxide. The experiments revealed the almost linear relationship between $\Delta R_f$ and abrupt of the conductivity.

![Figure 2](image2.png)

**Figure 2.** The PTSM width versus the thickness of the vanadium dioxide film.
The reflection jump $\Delta R_f$ grows with the film thickness that correlates with an increasing of the size of the crystallites [1].

4. Conclusion

The results show that the variation of thickness of the obtaining vanadium dioxide films significantly changes the parameters of the distribution of basic SMPT loops of the crystallites and thus optical performance of the samples. The most nonlinearity was obtained in the thick pyrolytic vanadium dioxide films.

The use of vanadium dioxide can be extended using heterogeneous material, consisting of a dielectric matrix (which is transparent in the infrared region of the spectrum) and microparticles with phase transition [10, 11]. This material enables the realization a volume hologram that it is impossible for pure vanadium dioxide due to the high absorption coefficient.

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