

Photothermal Depth Profiling on Vanadium Dioxide Photonic Crystals

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Vanadium dioxide is an interesting metal oxide which possesses thermochromism due to a semiconductor-metal phase transition at around $T_c=68^\circ\text{C}$. This feature is fundamental to develop a large variety of photonic devices: thermochromic “*smart*” window which autonomously controls sun rays into a room, thermally controllable localized-plasmon, hysteresis enhancement of a phase transition by nanoparticulation, optical memory by the means of phase transition, and ultrafast switching of the photonic stop band in photonic crystals. The aim of this work is to characterize three-dimensional opal-VO₂ photonic crystals with a photonic stop band in the visible range, with a wide thermal tunability of about 60meV within 10°C across T_c . A large variety of SiO₂/VO₂ opal samples with different diameter of the SiO₂-spheres and different infiltration of VO₂ were produced and characterized by using photothermal and photoacoustic techniques. First we applied photothermal deflection spectroscopy (PDS) at room temperature. The PDS spectra show a minimum in the absorbance in the visible range in perfect agreement with the maximum observed by using the Bragg reflectometry. From the spectra is also clearly visible a phase shift of about 10 degree which is related to a wavelength dependent shift of the VO₂ absorption centres. In other words when the structure is heated harmonically @25Hz, the thermal waves come out from the VO₂ layers where the e.m. field is more absorbed. In order to verify possible electromagnetic field localization effects, we applied also photothermal radiometry (PTR) so to perform an absorption depth profiling. In practice an Ar pump laser beam @514 nm is modulated by an acousto-optical modulator at a frequency ranging from 1 Hz up to 100 kHz, and focused onto the SiO₂/VO₂ opal structure. Since SiO₂ is not absorbing light @514nm the pump is absorbed only by the VO₂ crystallites distributed in the whole volume. Thermal waves are generated by all the VO₂ crystallites in the volume, and propagate back towards the sample surface. In practice, since the thermal waves are damped, only the long thermal waves can reach the surface and can contribute to the ac surface temperature rise which is measured by the infrared emission from the surface eventually detected by an infrared detector HgCdTe. Generally the IR signal is plotted as a function of modulation frequency from 1 Hz up to 100 kHz, which corresponds, for such opals, to a typical propagation distance m of the thermal waves from 400mm down to 1mm. Here it is crucial the comparison between the thermal diffusion length m and the optical absorption length $1/a$. This distinguishes the long thermal waves ($m>1/a$, low frequency) which can reach the surface from the short thermal waves ($m<1/a$, high frequency) not detectable at the surface. Theoretically in this range of frequencies the technique allows to measure the absorption length not shorter than 1mm. First a rough theoretical calculation estimates the effective absorption length in the SiO₂/VO₂ opals in the range 1.8mm -18mm depending on the filling factor (100 % ÷ 10 %), which is anyway above the thermal resolution of the system. In order to reconstruct more precisely the internal heat source profile the data have been inverted by using singular value decomposition. All the reconstructed profiles exhibit a typical quasi-exponential behaviour and are in excellent agreement with the numerical simulations of the light propagation in Photonic Crystals. The obtained optical penetrations obviously depend from the filling factor and from the diameter of the spheres. Similar measurements have been recently performed even at a higher room temperature so to investigate the semiconductor-metal phase transition and the consequent change in the absorption depth profile.