

**Annotation:**

By the Russian side of the project all announced tasks in preparation and studies of titanium dioxide thin films with incorporated ions of cobalt, vanadium or manganese have been done during the reporting period. Some of prepared films exhibit the ferromagnetic ordering at room temperature and could be considered as candidates to diluted magnetic semiconductors (DMS). Films have been prepared by direct doping with the impurity level up to several atomic percents. The doping has been done by rf magnetron sputtering method in the argon-oxygen atmosphere from metallic and/or ceramic (composite) targets with further vacuum annealing for several systems. The films have been tested by XRD, magnetometry (VSM, SQUID) and magneto-optical (MO) spectroscopy of transversal Kerr effect methods. Furthermore, the measurements of anomalous Hall effect (AHE), positron annihilation spectroscopy (PAS), absorption spectra (XANES) and fluorescence analysis (EDX) have been also done. PAS method allows to get information about the point and open-volume defects in the samples studied; EDX analysis could discover the presence of additional magnetic phases in the samples. For some films the values of magnetic moment per impurity atom have been calculated from the macroscopic magnetometry data.

The main interest of researchers was focused on TiO<sub>2</sub>:Co and TiO<sub>2</sub>:V thin films, that reveal an essential difference in their behavior: TiO<sub>2</sub>:Co films demonstrate either strong magnetization, MO response or AHE independently on presence or absence of magnetic Co clusters inside the films. Meantime, TiO<sub>2</sub>:V films show only tiny MO response or a total absence of it even for films with a recordable magnetization and the hysteresis loop. The AHE signal has not been recorded for any of TiO<sub>2</sub>:V films. It should be noted that MO spectra for TiO<sub>2</sub>:Co are significantly dissimilar for films with anatase or rutile matrix and differ strongly from MO spectra of nanocomposites films with cobalt clusters.

Researches involved in the project suggested the model for description of films behavior (and possible interactions inside them) that takes into account the magnetic polarization of presented oxygen vacancies (as other authors worked with DMS based on other systems).

Jointly with the German partner the summer school «Frontiers in TiO<sub>2</sub> based diluted magnetic semiconductors» has been held (Dresden, HZDR, September 11-15th, 2012) and two Internet-resources with an actual information about the project progress have been created (both in Russian and English).

***Initial goals for the Russian partner for the 2012:***

Initial goals of the Russian partner for the first year of the project (2012) have been formulated in the next points:

- preparation of TiO<sub>2</sub>:Co(5%) thin films by direct doping method like magnetron sputtering;
- preparation of TiO<sub>2</sub>:V and TiO<sub>2</sub>:Mn thin films with an impurity level in the range of 0.1÷10% (atomic percents) with an further annealing. It was assumed that TiO<sub>2</sub>:V and TiO<sub>2</sub>:Mn will reveal the ferromagnetic behavior;
- sample attestation by XRD for structure determination;
- sample attestation by VSM magnetometry for determination of the level of magnetic signal;
- measurements of magneto-optic (MO) and magneto-transport measurements for all producing samples and measurements of anomalous Hall effect (AHE);
- proposals preparation for a beamtime at the synchrotrons (ESRF and/or BESSY) for element-selective absorption (XAS) and magnetic circular dichroism (XMCD) experiments;
- jointly with the German partner the summer school at the HZDR was planned;

Up to the end of reporting period all announced tasks in preparation and studies of titanium dioxide thin films with doped 3d ions of cobalt, vanadium or manganese have been done.

***Obtained during 2012 results (main results):***

The thin films (~300nm) of titanium dioxide doped with 3d atoms of Co, V and Mn have been prepared by magnetron scattering in argon-oxygen atmosphere. Several of them exhibit the ferromagnetic ordering at room temperature and could be considered as diluted magnetic semiconductors (DMS). It has been found that:

- thin films TiO<sub>2</sub>:Co(0.5%, 1.3% and 5%) have either magnetization or MO signal of Transversal Kerr effect with the absence of magnetic clusters. It should be note, that MO signal significantly differ for films with anatase and rutile structure of TiO<sub>2</sub> matrix;
- thin films TiO<sub>2</sub>:Co(1%) exhibit magnetization, but MO spectra reveal the presence of magnetic clusters inside;
- thin films TiO<sub>2</sub>:V(3%, 5%) prepared from the metallic (and ceramic) targets reveal magnetization, but MO signal and AHE have not been found;
- for thin films of TiO<sub>2</sub>:Mn(5%) the ferromagnetic ordering at RT has not been found;
- for the sample TiO<sub>2</sub>:V(3%) the secondary phases have not been found, PAS method revealed only a tiny presence of point defects in the film;
- the calculated from magnetometry data magnetic moment per impurity atom for the TiO<sub>2</sub>:V(3%) from metallic target is about ~0.2÷0.4 $\mu_B$ .