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Titanium nitride room-temperature ferromagnetic nanoparticles

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ABSTRACT

Cubic and near-spherical TiN nanoparticles ranging in average size from 20 to 125 nm were prepared by levitation-jet aerosol synthesis through condensation of titanium vapor in an inert gas flow with gaseous nitrogen injection. The nanoparticles were characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD), BET measurements, UV–Vis, FT-IR, Raman spectroscopy, XPS, and vibrating-sample magnetometry. Room-temperature ferromagnetism with maximum magnetization up to 2.5 emu/g was recorded for the nanoparticles. The results indicate that the observed ferromagnetic ordering was related to the defect Ti–N structures on the surface of nanoparticles. This suggestion is in good correlation with the measured spectroscopical data.

1. Introduction

In the past decade the so-called "d^0 magnetics" have attracted great interest from physicists and chemists and were subject of many theoretical and experimental researches [1] due to their possible application in spin polarized carrier based devices [2]. d^0 magnetics is a class of materials, which lack magnetic ions and should, in principle, not be ferromagnetic, but, in fact, exhibit ferromagnetism at room temperature (RTFM) [3]. It has been reported that RFTM exists in thin films and nanoparticles of *undoped* oxides such as HfO_2 [4,5], ZnO [6,7], SnO_2 [8,9], In_2O_3 [8,10], CeO_2 [8,11], CuO_2 [12,13], MgO [14,15], CdO [16], TiO_2 [10,17]. Moreover, it has been suggested that structural defects, such as cation and oxygen vacancies, as well as structural inhomogeneity may induce ferromagnetic ordering [18]. RTFM is also exists in other inorganic materials with native surface defects. For example, RTFM phenomenon occurs in metal nitrides such as InN [19,20], GaN [21], NbN, MoN [22], TiN [23]. Among the metal nitrides, TiN is a subject of particular interest as it displays many other attractive features such as high hardness, good electrical conductivity, relatively high chemical inertness, very high melting point [24] and favorable optical properties [25,26]. TiN nanoparticles (NPs), which combine large surface areas with good electrical conductivity, should be ideal for use in super-capacitors [27,28]. Its chemical inertness and high melting point make it suitable for usage as a support in various heterogeneous reactions [29], including a catalyst support material for proton exchange membrane fuel cells [30,31]. Despite of many above mentioned advantages, observed value of room-temperature (RT) saturation magnetization of TiN NPs (0.002 emu/g) [23] is not enough for the real spintronic applications, which require materials with high-sensitivity to moderate magnetic fields [32].

It should be noted, that RTFM observations led to the idea of creating such magnetism by the manipulation of impurities as a consequence of structural and chemical inhomogeneity at the nanoscale [33]. Since it was observed in highly defective samples, it has led to the expectation, that magnetism may be the general property of such NPs [8]. Hence, it was obvious, that RTFM must be strongly dependent from the method of its production. In our previous papers we reported that some undoped oxide-based NPs, synthesized by using levitation-jet generator, demonstrated larger

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values of maximal saturation magnetization than nanoparticles, fabricated by using other experimental techniques: Zn–O – 0.27 emu/g [7] (0.01 in Ref. [34]), Sn–O – 0.10 emu/g [9] (0.02 in Ref. [35]), Cu–O – 0.06 emu/g [13] (0.01 in Ref. [12]). Earlier, some manipulations with manufacturing conditions of SiC single crystals have resulted in RTFM enhancement. In 2011 Liu et al. observed very low net RTFM magnetization after neutron irradiation treatment of SiC single crystals [36]. After proton irradiation treatment of such compound RTFM maximal magnetization value of up to 0.7 emu/g was found [37]. After Ne bombardment RTFM of up to 3 emu/g (normalized to the implanted mass) at 5 K was also established [38].

In order to synthesize the nanocrystalline TiN powder a benzene thermal route was proposed by Hu et al. [39]. However, the possible danger of the preparation procedure using high-temperature organic solvents make it impossible to be used in the real practice. A long-time nitridation (for 5 h at 800 °C) of nanocrystalline TiO_2 powder yield *spherical* TiN NPs [40]. Un-coagulated TiN NPs have been synthesized in a complicated arc plasma torch based reactor, with precursor-laden plasma beam expanding supersonically into an evacuated chamber [41]. *Cubic* NPs were prepared by evaporating of Ti metal in the N_2 atmosphere, by employing a modified arc discharge method [42]. Similar TiN NPs were produced using a dual plasma system based on Ti ablation from a pulsed low pressure arc plasma, expanding in a capacitively coupled RF glow discharge sustained in an Ar/N_2 mixturing atmosphere [43]. A supersonic thermal plasma expansion process has been exploited for the synthesis of cubic-shaped TiN NPs by injecting $TiCl_4$ and NH_3 continuously to the hot and cold tail zones of the plasma jet [27]. A small amount of size-selected TiN NPs were produced by ionized cluster beam deposition method [44]. A mixture of cubic-shaped and spherical TiN NPs were synthesized through the electrical explosion of Ti wire using nitrogen gas under the different pressure [45]. It should be noted that above-mentioned TiN nanoparticles were not investigated from the point of view of their magnetic properties. To our knowledge only Gong et al. observed slight RTFM for the TiN NPs with an average particle size of 20–50 nm prepared by calcinations of nanotubular titanic acid in the flowing ammonia [23].

We tried to obtain larger magnetization values in TiN nanoparticles of various sizes by using gaseous nitrogen injection in an inert gas flow of levitation-jet generator at ambient pressure. Such crucible-free technique offered large difference in the experimental conditions in case of RTFM TiN NPs, which were obtained by using other known techniques. In particularity, it provides an easy controlling method over the size, morphology and composition of aerosol-generated nanoparticles. Due to the self-purification effects at the beginning of the evaporation process, volatile impurities in the Ti metal have time to release to the condensation zone, whereas the refractory impurities are permanently collected in the evaporated droplet [46].

In present paper, we focus on the interrelation between the development of RTFM as well as on the structural and optical properties of TiN nanoparticles, exhibiting RTFM. Nevertheless, precise mechanism behind the reported RTFM is not well understood and is a subject of discussion. It received a considerable boost by the metal oxide and nitride, invoking that physics, underlying this phenomenon, is universal [47]. The present study may provide useful clues for understanding the origin of RTFM.

2. Experimental

2.1. NPs synthesis conditions

TiN aerosol-generated nanoparticles (NPs) were obtained by using modified Gen levitation-jet generator described in detail elsewhere [46] (see also Fig. S1 in Appendix A. Supplementary Material (SM)). In this technique a titanium droplet (purity is 99.55 at.%) suspended in an appropriate quartz tube. The droplet was heated up by electromagnetic field generated using a counter-current inductor until the levitated metal began to vaporize. The vaporizing liquid droplet was blown down by an adjustable stream of Ar (99,998 at.%) or He (99.995 at.%) and supplied by Ti wire (0.4 mm in diameter) at constant feed speed. In all the experiments, special actions were undertaken for the metal nitridation. In this way an amount of gaseous nitrogen (99,996 at.%) was added in the basic flow in the split or combined modes [46]. After finishing of all the above-mentioned processes, the resultant brown powder was collected on the cloth filter and hereinafter removed from it into a particle container. It should be noted, that immediately after the generator was turned off, the thrown droplet already has a characteristic gold-color, indicating an existence of TiN coating on its surface. During the synthesis itself, appropriate measures were undertaken, in order to prevent any influence of alien magnetic contaminants.

All the obtained NPs were divided on the three groups depending on the applied gas flow modes. The first group of NPs were obtained when the nitrogen gas was injected in Ar based flow in the split-regulated mode (SRA), where the space between lower N_2 input and bottom of the levitated droplet h_s could be changed. For the second group of NPs combined mode was used, when nitrogen gas was added into Ar based flow through an upper input (CA). In the third case nitrogen gas was added into He based flow in the combined mode through the upper input (CH). Specificity of all the synthesis conditions were determined with the aim to change the extent of nitridation in the final product. In the first case, no real N_2 gas flow limit was observed. The maximum allowed nitrogen input flow value in the second and third cases was limited by increasing an excess of liquid metal droplet surface nitridation, which results in termination of the evaporation process due to solidification of the droplet. All the parameters of NPs synthesis, including titanium metal feed rate, inert and nitrogen gas flows rates are listed in Table 1.

2.2. Characterization of NPs

The NPs morphology, dimensions and chemical composition were examined using scanning electron microscope CARL ZEISS ULTRA PLUS/INCA ENERGY 350. Specific surface area of NPS was determined by 4-point nitrogen physical sorption BET measurements using META SORBI-M device. Crystal structure of NPs was studied by X-ray powder diffractometer DRON-3M (Cu K_α radiation). Their phase composition was determined using JCPDS PDF database (release 2011) and Crystallographica SearchMatch ver. 3.102 software. Rietveld analysis (PowderCell for Windows ver. 2.4) of X-ray diffraction patterns was used to evaluate the ratio of crystalline phases in the NPs. UV–vis spectra were recorded using Lambda950 (Perkin Elmer) with integrated sphere detector. Fourier transform infrared (FT-IR) spectra were recorded in solid phase using Tensor 27 spectrometer with attenuated total reflectance accessory (Bruker) in the frequency range of 400–4000 cm^{-1}. Raman spectra were recorded at room temperature using InVia Raman Renishaw and confocal microscope Leica DMLM apparatus with an air-cooled, charge coupled device and coupled with Ar laser emitting at 514.5 nm. Maximum laser power of 55 μW (100%) was applied to the samples inside of 2 mm diameter spot through the standard ×50 microscope objective. XPS results was obtained by using Thermo Scientific X-ray Photoelectron Spectrometer equipped with monochromated Al K_α (1486.6 eV) source running at 72 W with a pass energy of 50 eV. One point scale with the C 1s peak (C–C