Tunning Titanium Oxynitride Nanoribbons Conductivity Properties: Synthesis and Characterization

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Transition metal oxynitrides are important functional materials for a wide spectrum of applications such as photocatalysts, pigments, dielectric and magnetic materials. They can combine the properties of transition metal oxides and nitrides, and are typically prepared thermally by nitridation of metal oxide where nitrogen or ammonia gases are used as a nitrogen source. The substitution of oxide anions with nitride ones in metal oxides enables the fine tuning of oxynitride properties.

In our work, this paradigm was applied to formation of titanium oxynitride (Ti(O,N)) nanoribbons, transformed from hydrogen titanate (H2Ti3O7) nanoribbons by heating in a dynamic ammonia atmosphere. The effect of reaction conditions, NH3(g) flow and reaction time, on magnetic properties, resistivity and morphology of the prepared samples was investigated. Structural and morphological properties of the products were characterized with X-ray diffraction and electron microscopy techniques (TEM, SEM, HRTEM). Elemental composition was determined by means of X-ray photoelectron spectroscopy. Magnetic properties of the products were measured with a SQUID magnetometer, while the temperature dependence of the resistivity of individual nanoribbons was measured with a four point method.

The transformation of H2Ti3O7 to Ti(O,N) proceeds in two stages, first H2Ti3O7 transforms to TiO2 and in the second stage the nitridation stage é TiO2 converts to Ti(O,N). As revealed by SEM images the nanoribbon shape stays preserved but the nanoribbons became porous. The appearance of porosity could be a consequence of the Kirkendall effect. The nitrogen content, which determines the chemical disorder through random O/N occupancy and ion vacancies in the Ti(O,N) composition, increases with the reaction time. The presence of disorder has paramount effect on resistivity of Ti(O,N) nanoribbons.

Atypically for metals, the resistivity increases with decreasing temperature due to the weak localization effects. From this state, superconductivity develops below considerably or completely suppressed critical temperatures, depending on the disorder strength. Our results thus establish the remarkable versatility of anion exchange for tuning of the electronic properties of Ti(O,N) nanoribbons and suggest that similar strategies may be applied to a vast number of nanostructures. (1)

[1] M. Sluban, P. Umek, Z. Jaglicic, J. Buh, P. Smitek, A. Mrzel, C. Bittencourt, P. Guttmann, M.-H. Delville, D. Mihailovc, D. Arcon, *ACS Nano* **9**, 10133 (2015).