



Defects-Driven Ferromagnetism in Undoped Dilute Magnetic Oxides: A Review



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In the past several decades, dilute magnetic semiconductors, particularly the dilute magnetic oxides have evolved into an important branch of materials science due to their potential application in spintronic devices combining of properties of semiconductors and ferromagnets. In spite of a major effort devoted to the mechanism of ferromagnetism with a high Curie temperature in these materials, it still remains the most controversial research topic, especially given the unexpected *d*⁰ ferromagnetism in a series of undoped wide-band-gap oxides films or nanostructures. Recently, an abundance of research has shown the critical role of various defects in the origin and control of spontaneous magnetic ordering, but contradicting views from intertwined theoretical calculations and experiments require more in-depth systematic research. In our previous work, considerable efforts have been focused on two major oxides, i.e. ZnO and ZrO₂. This review will present a summary of current experimental status of this defect-driven ferromagnetism in dilute magnetic oxides (DMOs).

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1. Introduction

Nowadays, people take advantage of the charge of electrons in semiconductors integrated circuits (ICs) for information processing and transmission, thanks to their high speed signal processing and good reliability, but the memory elements are volatile. People utilize the spin of electrons for information storage in magnetic materials because they are non-volatile despite slow read and write speeds. With a significant increase in demand for non-volatile, low-power and high-speed memories, researchers from the globe try to make use of both charge and spin of electrons at the same time, making it a challenging field due to its potential application for spintronic devices, such as the spin qubits for quantum computers, spin field effect transistors (spin-FETs), and spin light-emitting diodes (spin-LEDs)^[1–5]. A hardest challenge in the above devices based on spins and charges is that the material should be ferromagnetic above room temperature (RT) and have both efficient spin-polarized carrier injection and transport^[4]. However, the reported spin injection efficiency is usually too low, less than 1% with ferromagnetic metals employed as the contacts, due to the large density of states (DOS) mismatch between a metal and semiconductor^[6,7]. Making use of ultrathin MgO or Al₂O₃ layers as tunnel barriers has partially

alleviated the issue, which raised the injection efficiency to about 30%^[8,9]. However, it still cannot meet the request for practical application. For this reason, developing functional ferromagnetic semiconductors as spin-injection contacts working at RT seems to be imperative because they have high-quality interfaces to semiconductors and do not have the conductivity mismatch problem, and has attracted considerable attention for several decades^[10].

Earliest research efforts in this field were focused on natural magnetic semiconductors (Fig. 1(a)), such as rock-salt Eu- and Mn-based chalcogenides, in 1960s, but the low Curie temperature and conductivity limited their practical application^[11]. The discovery of ferromagnetism in II–VI (CdTe) and III–V (GaAs) compound semiconductors doped with magnetic impurities (Mn) in 1990s made dilute magnetic semiconductors (DMSs) a cutting-edge field^[12]. The term DMS refers to a non-magnetic semiconductor wherein a homogeneous dilute concentration of a magnetic dopant (with a net spin moment) is dispersed (Fig. 1(b)), and the resulting materials exhibit ferromagnetism. However, most of them also have a low Curie temperature and are difficult to synthesize and dope, which limit their interest. A major breakthrough that focused attention on wide-band-gap semiconductors as being the most promising for achieving practical magnetic ordering temperatures came with the theoretical prediction of room temperature ferromagnetism (RTFM) for 5 at.% Mn doping in GaN diamond and ZnO (see Fig. 2) by Dietl et al.^[13]. The theoretical studies were the first step to dilute magnetic oxides (DMOs) and then many groups started to work in this field. The report of RTFM in Co doped TiO₂ films has obviously

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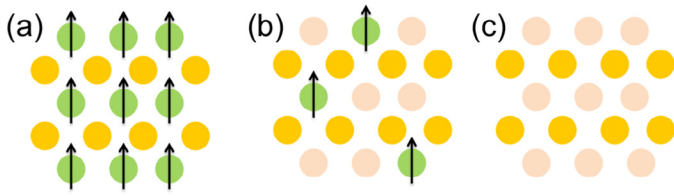


Fig. 1. Different types of semiconductors: (a) magnetic semiconductor; (b) dilute magnetic semiconductor; (c) non-magnetic semiconductor^[1].

encouraged experimental studies^[14]. Since then, intense research efforts have followed on these to realize robust RTFM in doped oxide materials and many wide-band-gap oxides, such as ZnO^[13,15–20], TiO₂^[14,21–24], SnO₂^[25–29], In₂O₃^[30–34], SrTiO₃^[35–38], etc. People understood that the RTFM resulted from the interaction between the dopant moments and carrier spins with different theoretical models such as RKKY^[39,40], mean field theory^[13,41,42], or double exchange^[43,44] etc., and considered that doping played a key role in the RTFM of DMOs^[45]. However, the observation of RTFM in undoped HfO₂ thin films^[46–48] by Coey et al. made the understanding of RTFM in DMOs more controversial. Neither Hf⁴⁺ nor O²⁻ are magnetic ions, and the *d* and *f* shells of Hf⁴⁺ ions are either empty or full, so called *d*⁰ magnetism^[49], which challenges our basic understanding that magnetic order in an insulator required the cation to have partially filled shells of *d* or *f* electrons. Triggered by the unexpected results, many groups have made considerable efforts to investigate the possible origin of RTFM in these undoped DMOs.

Given the high sensitivity of the observed RTFM in most DMOs to the growth conditions, researchers considered that the various intrinsic defect states (point or extended) must play a major role after tremendous theoretical and experimental work. Up to now, different kinds of intrinsic defects have been reported to be responsible for the RTFM in undoped DMOs^[50–53], such as structure defects, surface defects, strain, and point defects like vacancies and interstitials, leaving it still an open question. In the last several years, our research group has also paid considerable attention on the RTFM in undoped DMO semiconductors and insulators, such as ZnO^[54–58] and ZrO₂^[59,60]. Thorough analysis and characterization indicate that the ferromagnetism is induced and driven majorly by oxygen vacancy within the DMOs. Here, we present a brief review of the experimental work, which is divided into three parts. First, a brief introduction will be given about several methods used to analyze

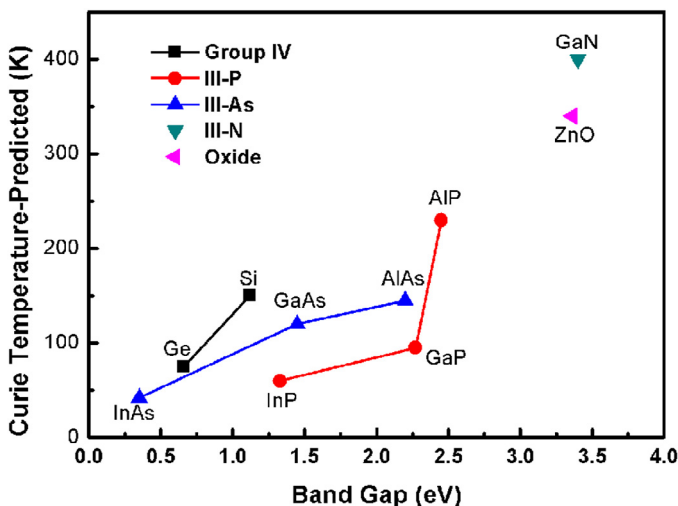


Fig. 2. Predicted Curie temperatures in oxides and semiconductors^[13].

and characterize defects. Then some results on the defect-driven ferromagnetism will be present, corresponding to the two major research objects in the second and third sections, respectively. At last, a discussion and some conclusions on defect-driven ferromagnetism in undoped DMOs will be given.

2. Defect Analysis and Characterization in DMOs

Various types of intrinsic defects are very common in oxide thin films prepared by various non-equilibrium methods. Characterizing the physical, chemical and crystallographic states is the necessary work when one wants to investigate the defect-related property. People usually take advantage of indirect effects of defects in solids, such as electrical, optical, acoustic, and so on, to characterize them, since direct analysis is too difficult to achieve. Here is a brief introduction on several methods of defect characterization utilized in our research.

2.1. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is one of the surface-sensitive quantitative spectroscopic techniques measuring the elemental composition, empirical formula, and chemical state of the elements. It is obtained with a beam of X-ray by irradiating a metal (usually Mg or Al) while simultaneously measuring the kinetic energy and number of electrons escaping from the surface (0–10 nm) of the material. By a survey scan, one can know whether some certain elements exist or not within the material, and obtain the stoichiometric ratio by calculation from the survey spectra roughly. To get more details of a certain element, one can conduct a high resolution core level scan and further peak-fitting, thanks to the high sensitivity of binding energy to the chemical environment. Taking oxygen (O) for instance, one can obtain signs of oxygen vacancy (V_O) from the O1s core level spectra if the peak shifts to higher binding energy slightly. Imagining the oxygen ions in the oxygen-deficient regions, the two electrons weakly bound by V_O can be partially and fully ionized, thus decreasing the electron charge density around the V_O regions and resulting in less screening of the O²⁻ 1s electrons from their nucleus, which raises the effective nuclear charge and the binding energy of an O²⁻ 1s electron^[61,62]. Besides the core level spectra, Auger peak in XPS spectra can also provide some clues on defects, and is reported to be much more sensitive to the chemical environment than core level peak for some metal elements^[63,64]. In addition, one can also obtain the distribution of elements or defects along the growth direction by XPS depth profile analysis, which can help to grasp the development and evolution of defects during the growth process.

2.2. Positron annihilation spectroscopy

Positron annihilation spectroscopy (PAS) is a kind of non-destructive spectroscopic techniques to study defects in solids. It operates on the principle that positrons, when injected into a solid, will annihilate through interaction with electrons, which releases gamma rays that can be detected. For solids containing free electrons (such as metals or semiconductors), the injected positrons annihilate rapidly unless there are some vacancy defects, especially negative charged vacancy. That is because that the positrons will reside in the vacancy defects, if they are available, and annihilate less rapidly than that in the bulk of the material. By analyzing the positron lifetime, which is between the emission of positrons from a radioactive source and the detection of gamma rays due to annihilation of positron annihilation, one can obtain some clues on the defects due to the dependence of lifetime on the type of vacancy defects^[65].

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