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On the understanding of the microscopic origin of the properties of diluted magnetic semiconductors by atom probe tomography

R.K. Zheng[a,*], M.P. Moody[a], B. Gault[a], Z.W. Liu[a], Hui Liu[b], S.P. Ringer[a]

[a]The Australian Key Centre for Microscopy and Microanalysis, The University of Sydney, New South Wales 2006, Australia
[b]Department of Electronics, College of Information Technical Science, Nankai University, Tianjin 300071, People's Republic of China

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Abstract

Spintronics, in which both the spin and charge of electrons are used for logic and memory operations, promises to revolutionize the current information technology. Just as silicon supports microelectronics, diluted magnetic semiconductors (DMSs) will be the platform of spintronics. Ideal DMSs should maintain ferromagnetic and semiconducting properties at operating temperatures to realize the spintronic functions. Although many high-temperature Curie temperature DMSs have been reported, the origin of ferromagnetism remains controversial. Currently, this is a major obstacle to the development of spintronic devices. The solution to this problem depends on a more complete understanding of DMS microstructure, especially the distribution of doped magnetic ions at atomic resolution and any defects introduced. Therefore, an analysis technique is required, possessing both high spatial and elemental resolutions, which is beyond the capability of conventional techniques, such as electron microscopy. However, atom probe tomography (APT), which recently has been successfully applied to nanoscale characterization of structural materials, has the potential to provide the unique combination of near atomic spatial and elemental resolutions needed for such an investigation.

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1. Spintronics and diluted magnetic semiconductors

It has been argued with considerable justification that the last half of the 20th century could be called the microelectronics era [1]. However, microelectronics is reaching the end of the so-called silicon road map due to the insuperable physics and materials challenges [2,3]. Spintronics, in which both the spin and charge of electrons are used for logic and memory operations, offers a possible solution for the next generation of information technology [1,2].

One of the major technical barriers that must be overcome to realize the practical implementation of spintronic devices is the development of suitable spin-polarized materials that will effectively allow spin-polarized carriers to be injected, transported, and manipulated [4]. One category of materials that exhibits large carrier spin polarization is half-metals [5], in which the Fermi level intersects only one of the two spin bands, whereas for the other spin band the Fermi level resides in a band gap. Therefore, half-metals have a spin polarization of as high as 100%. The major drawback of these spintronic materials is that they are so conductive that they cannot be incorporated into semiconductor devices due to the large conductivity mismatch between ferromagnetic half-metals and semiconductor materials. The alternative approach is to create spin polarization in semiconductors. The semiconductors used for current devices and integrated circuits are not spin polarized. In order to obtain high spin polarization, the spin up and down bands are split by introducing magnetic elements into nonmagnetic semiconductors to make them magnetic. This category of new materials is called diluted magnetic semiconductors (DMSs) [6]. The magnetic exchange interaction will split the spin up and down bands, like in ferromagnets. Due to

*Corresponding author. Tel.: +61 2 9351 7542; fax: +61 2 9351 7682.
E-mail address: rzheng@usyd.edu.au (R.K. Zheng).

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the merit of electronic band structures of semiconductors, a small split of electronic bands can lead to 100% spin polarization, as shown in Ref. [7, Fig. 1A]. The advantages of DMSs are their potential as spin-polarized carrier sources and easy integration into semiconductor devices. It should also be noted that pure semiconductors have been proposed as possible materials for spintronics [8,9].

Although ferromagnetic semiconductors had been studied about half a century ago, it is only after the breakthrough work by Ohno et al. on (In,Mn)As [10,11] and especially (Ga,Mn)As [12,13] that DMSs drew intensive interest from scientific and industrial communities. Previously, Coey identified a set of key criteria for an ideal DMS [14]: (i) Curie temperature >500 K; (ii) a close connection between the ferromagnetism and the population of a spin-split band of carriers [15,16]; (iii) a choice of p or n type doping; (iv) high mobility and long-spin diffusion length, needed for lateral heterostructures [17]; (v) magneto-optic effects including magnetic circular dichroism [18]; (vi) anomalous Hall effect [12,13]. It is apparent from the references listed above that all the criteria are met except for the Curie temperature, which is still well below 500 K. Dietl et al. predicted Curie temperatures for several classes of these materials via theoretical calculation [15]. According to the famous table in Ref. [15], among the candidates, GaN and ZnO could maintain ferromagnetism above room temperature by proper Mn doping. Owing to recent intensive studies, quite a few DMSs above room temperature have been discovered, such as Mn-doped $CdGeP_2$ [19], (Ga,Mn)N [20,21], (Ga,Mn)P [22], (Zn,Mn)O [23], (Ti,Co)O_2 [9,24], (Sn,Co)O_2 [25]. However, the origin of ferromagnetism in the DMSs is very controversial [8,9,25–47].

2. Controversy in experimental observations

One of the most intensively studied candidates is GaN [47], since it was predicted to be a room-temperature DMS [15]. Reed et al. achieved a Curie temperature in the range of 228–370 K in manganese-doped GaN [20]. They did not find secondary magnetic phases from structure characterization by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Sonoda et al. reported that wurtzite-structured (Ga,Mn)N films showing ferromagnetic behavior at room temperature were successfully grown on sapphire(0 0 0 1) substrates by molecular beam epitaxy using ammonia as a nitrogen source [21]. They found that the magnetic-field dependence of magnetization of a (Ga,Mn)N film at 300 K was ferromagnetic, while a GaN film showed Pauli paramagnetism-like behavior. Further, they estimated that the Curie temperature of a (Ga,Mn)N film was as high as 940 K. Very recently, Yoshi et al. again observed ferromagnetism above room temperature in 8.2% Mn-doped GaN by molecular beam epitaxy. They found that the high-temperature ferromagnetic state is significantly suppressed below 10 K, accompanied by an increase of the electrical resistivity with decreasing temperature. So they believed the high-temperature ferromagnetism is carrier-induced.

However, ferromagnetism was absent in many reports [48–50]. Ando studied (Ga,Mn)N film with X-ray magnetic circular dichroism (XMCD). The results indicated that $Ga_{1-x}Mn_xN$ is a paramagnetic DMS. The room-temperature ferromagnetism of the sample arises from an unidentified material, instead of $Ga_{1-x}Mn_xN$, that is not detected by the XRD. These results show that the magneto-optical spectroscopy is indispensable to confirm the intrinsic ferromagnetism of DMS [51]. Zhang et al. investigated (Ga,Mn)N prepared by different methods [52]. In a systematic study, they found that room-temperature ferromagnetism was observed only in polycrystalline or amorphous (Ga,Mn)N, and not in single-crystalline state. This indicates that room-temperature ferromagnetism is related to the grain boundaries, surface/interface, or other defects.

Wierzbowska et al. compared the different origins of the ferromagnetic order in (Ga,Mn)As and (Ga,Mn)N [38]. They found a hole-mediated picture of the ferromagnetism in (Ga,Mn)As, but double-exchange mechanism caused ferromagnetism in wurtzite (Ga,Mn)N, which suggests a two-phase picture of the ferromagnetic order in (Ga,Mn)N, with a robust ferromagnetic phase at large Mn concentrations coexisting with a diluted weak ferromagnetic phase. Sato et al. also found that the range of the exchange interaction in (Ga,Mn)N is very short, but the interaction is weaker but long ranged in (Ga,Mn)As. Monte Carlo simulations show that the Curie temperatures of (Ga,Mn)N are very low since percolation is difficult to achieve for small concentrations and the mean field approximation strongly overestimates Curie temperatures [42].

ZnO is another widely studied DMS candidate [47,53,54]. Although theoretical calculation predicted that only p-type (Zn,Mn)O leads to ferromagnetism [15,23], ferromagnetism in insulating (Zn,Mn)O [55] and n-type (Zn,Mn)O [23,56,57] have been experimentally observed by different research groups. Kundaliya et al. have demonstrated that the ferromagnetism in their (Zn,Mn)O originates in a metastable phase rather than by carrier-induced interaction between separated Mn atoms in ZnO [46]. The ferromagnetism persists up to similar to 980 K, and further heating transforms the metastable phase and kills the ferromagnetism. They also found that a uniform solution of Mn in ZnO does not form under low-temperature processing. Instead, a metastable ferromagnetic phase develops by Zn diffusion into the Mn oxide. Their results strongly suggest that the observed ferromagnetic phase is oxygen-vacancy-stabilized $Mn_{2-x}Zn_xO_3$ [28,46].

High-temperature ferromagnetism was also reported in insulating (Zn,Co)O films [58]. By XMCD measurements, Ando et al. [51,59,60] suggested that (Zn,Co)O is suitable as a DMS material, albeit the p–d exchange interaction is antiferromagnetic. However, antiferromagnetism [61,62] and spin glass behavior [63,64] were also found to be in