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2004 J. Phys.: Condens. Matter 16 S5705

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# Enhancement of $T_C$ by a carrier codoping method with size compensation for nitride-based ferromagnetic dilute magnetic semiconductors

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Received 15 April 2004

Published 19 November 2004

Online at [stacks.iop.org/JPhysCM/16/S5705](http://stacks.iop.org/JPhysCM/16/S5705)

doi:10.1088/0953-8984/16/48/032

## Abstract

Based on *ab initio* calculations of electronic structures of Mn-doped GaN, a carrier codoping method with size compensation to enhance the Curie temperature ( $T_C$ ) of GaN-based dilute magnetic semiconductors is proposed. Beryllium (Be) is chosen as a codopant to reduce the volume expansion caused by Mn doping, and also to enhance the 3d-density of states at Fermi level by hole doping. It is found that the mid-gap impurity band is strongly broadened due to strong p–d hybridization, resulting in a considerable increase of the hole density. With Be substituting both the cations and anions, the reduction of the antiferromagnetic super-exchange interaction in the regime of high Mn-concentrations and the highest value of  $T_C$  due to the ferromagnetic double exchange interaction are strongly expected.

## 1. Introduction

The discovery of ferromagnetic dilute magnetic semiconductors [1] (DMS) by incorporating the transition metals (TM) into various host semiconductors has received much attention because of the potential applications that simultaneously employ the charge and spin of the carriers in control of the electronic properties of materials. From the viewpoint of industrial application, the magnetic ordering of DMS must be achieved in a temperature higher than room temperature. Hence, to synthesize materials with a Curie temperature ( $T_C$ ) higher than room temperature has become an important issue in spintronics.

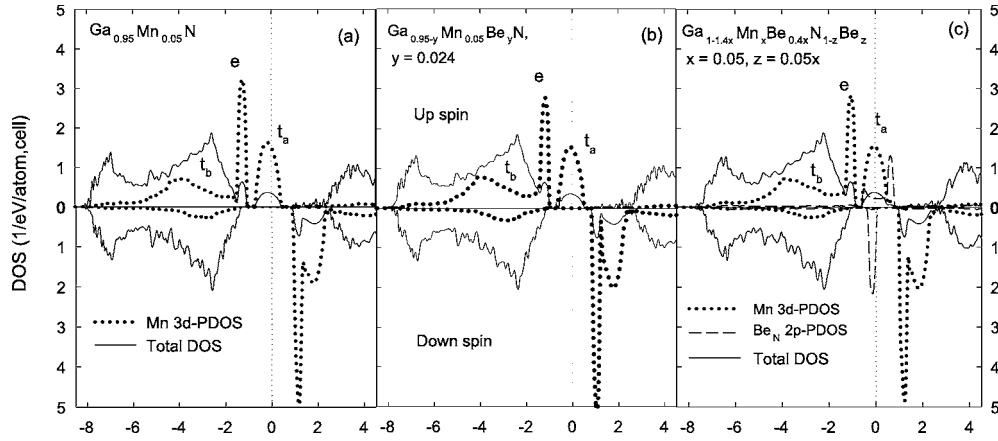
GaN and related semiconductors are treated as key advanced materials for spintronic devices because they have a wide band gap, exhibit very high optical efficiencies, and can be used in electronic devices such as high power and high frequency transistors, blue

and ultraviolet (UV) light-emitting diodes, laser diodes, etc. Furthermore, the stability of the ferromagnetism of (Mn, Cr, V)-doped nitrides at temperatures higher than room temperature [2–7] predicted by theoretical calculations and reported experimentally suggests a promising possibility of using these materials for spintronic device applications. However, theoretical calculations show a drop of  $T_C$  in the regime of high Mn concentrations ( $x > 0.08$ , where  $x$  denotes the Mn concentration) due to the antiferromagnetic super-exchange interaction. Moreover, similarly to  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ , the volume expansion is caused by Mn substituting Ga in wurtzite GaN. The predominant secondary phase which forms in bulk  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  was shown by molecular beam epitaxy experiments to be  $\text{Mn}_x\text{N}_y$  (in particular,  $\text{Mn}_3\text{N}_2$ ). Important questions arise about how to reduce the volume expansion and the formation of a secondary phase, and how to increase the hole density for the enhancement of  $T_C$ . For  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ , we have proposed a new codoping method to enhance the solubility of substituting Mn by reducing the interstitial Mn. In this method, carbon (C) (or nitrogen (N)) is chosen as the codopant substituting As with concentrations satisfying the condition of size compensation [8]. A similar codoping method can be considered to apply to  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ . It is noted that while an enhancement of  $T_C$  by codoping N or C into  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  was reported experimentally by Kling *et al* [9] and Park *et al* [10], experimental results by Yu *et al* show Fermi-level-induced hole saturation and an increase of the concentration of Mn interstitials, and hence a drop of  $T_C$  of  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{As}$  [11]. The *ab initio* calculations show that the relaxations caused by Mn doping in  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  are quite small [12]; therefore the incorporation of Be, which has an ionic radius much smaller than Ga, into  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  can lead to a fraction of substitutional Mn being kicked out of the Ga sites to occupy the interstitials or to form random clusters, resulting in the compensation of the hole and a drop of  $T_C$ , as shown in [11]. Moreover, the Fermi level in  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  is quite close to the valence band. Hence, codoping Be with sufficiently high concentrations into  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  can introduce a shift of the Fermi level into both valence bands of up and down spins, resulting in a compensation of spins at the Fermi level. Fortunately, such a behaviour is hard to appear in  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ . By substituting Ga by Mn, the nearest neighbour N atoms in  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  can be shifted 3% outward [12, 13]; the volume expansion is much stronger than that of  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ . Furthermore, in  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  the Fermi level lies deeply in the band gap; the codoping Be (substituting Ga) does not lead to spin compensation. Therefore, Be can be considered as the best codopant to reduce the lattice expansion caused by Mn doping and to enhance the charge carrier concentration of  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ .

In this paper, we propose a codoping method to enhance the  $T_C$  of  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ . Be is chosen as the codopant, and its concentrations are adjusted so that the volume expansion caused by Mn doping is compensated. The density of states (DOS) of  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ,  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$  and  $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$  are calculated. The  $T_C$  values within the mean field approximation (MFA) of these compounds are evaluated.

## 2. Calculation results: density of states and Curie temperature

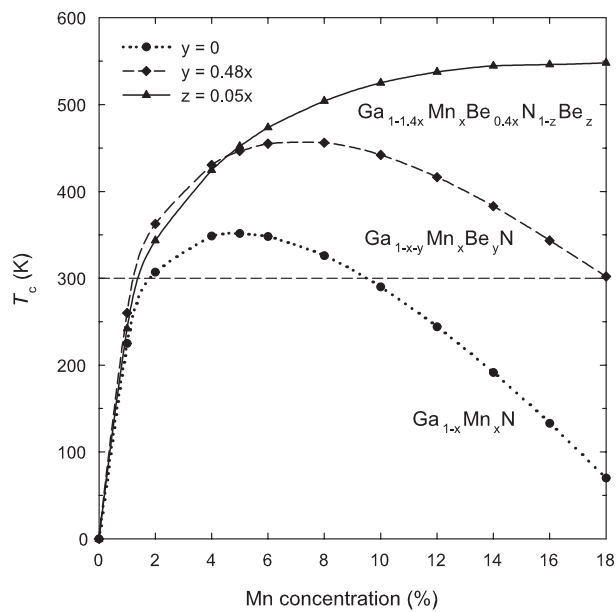
The DOSs are calculated based on the KKR-LSDA-CPA method [14] for three cases of doping:  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ,  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$  and  $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$ . To synthesize GaN-based DMS, Ga atoms in wurtzite GaN are randomly substituted by Mn atoms. The  $T_C$  is evaluated by using the mean field approximation [3]. To simulate the spin-glass states of the above-mentioned compounds, Ga cations are substituted randomly by  $\text{Mn}_{x/2}^\uparrow$  and  $\text{Mn}_{x/2}^\downarrow$  magnetic ions, where  $\uparrow$  and  $\downarrow$  denote the direction of the local moment of the Mn ions. The ferromagnetic and spin-glass states of GaMnN can be described as  $\text{Ga}_{1-x}\text{Mn}_x^\uparrow\text{N}$  and  $\text{Ga}_{1-x}\text{Mn}_{x/2}^\uparrow\text{Mn}_{x/2}^\downarrow\text{N}$ , respectively. Throughout the calculations, the potential form is restricted to the muffin-tin



**Figure 1.** Total DOS per unit cell (solid curve), and PDOS of 3d-states per Mn atom at the Ga site (dotted curve) at 5% of Mn concentrations for  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ,  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$  ( $y = 0.48x$ ) and  $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$  ( $z = 0.05x$ ).

type, and the wavefunctions in each muffin-tin sphere are expanded with real harmonics up to  $l = 2$ , where  $l$  is the angular momentum at each site. 456  $k$ -points in the irreducible part of the first Brillouin zone are used. The relativistic effect is also taken into account by using the scalar relativistic approximation. In order to reduce the volume expansion due to Mn doping, concentrations of Be are estimated based on the following ionic radii: 0.47 Å (Ga), 1.4 Å (N), 0.65 Å (Mn) and 0.27 Å (Be). For comparison, three cases of doping are considered for various concentrations of Mn: the single doping  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ , codoping  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$ , and  $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$ . In the last case, concentrations of Be substituting for Ga cations are chosen to be  $0.4x$  (where  $x$  denotes the Mn concentration) so that the Mn 3d-partial density of states (PDOS) at the Fermi level can reach the highest values. In order to compensate the volume expansion, a very few Be atoms ( $z = 0.05x$ ) are also chosen to substitute for N anions.

Figure 1 illustrates the DOS of  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  (a),  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$  (b) and  $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$  (c) for  $x = 0.05$ . As shown in the figure, the anti-bonding states  $t_a$  of 3d-Mn of all three cases hybridize with N 2p-states to make a wide impurity band. This band is broadened with increasing Mn concentration. For the cases of codoping with Be ((b) and (c)), the Fermi level shifts towards the valence band, resulting in the increase of the hole density. Furthermore, the peak of the antibonding state ( $t_a$ ) is located near the Fermi level. Hence, the 3d-PDOS at Fermi level  $n_{3d}(E_F)$  is gradually enhanced. When Be atoms substitute for both kinds of sites (c), the  $t_a$ -peak lies at the Fermi level. Moreover, since Be substituting for N ( $\text{Be}_N$ ) acts as a triple acceptor, the appearance of the  $\text{Be}_N$  2p-states at the Fermi level for up spins leads to the enhancement of the hole density at  $E_F$  and the strong broadening of the mid-gap impurity band. For DMS, in which the double exchange mechanism is dominant,  $T_C$  is proportional not only to  $n_{3d}(E_F)$  but also to the width of impurity band  $W$  ( $T_C \propto Wn_{3d}(E_F)$ ). Therefore, the  $T_C$ s of  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$  and  $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$  are enhanced in comparison with that of  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ , as shown in figure 2. Additionally, as distinct from the case of  $\text{Ga}_{1-x-y}\text{Mn}_x\text{Be}_y\text{N}$  (b), the antiferromagnetic super-exchange interaction [3] in  $\text{Ga}_{1-x}\text{Mn}_x\text{N}$  is strongly reduced with Be substituting for both kinds of sites ( $\text{Ga}_{1-1.4x}\text{Mn}_x\text{Be}_{0.4x}\text{N}_{1-z}\text{Be}_z$ ) (c). Therefore, the decrease of  $T_C$  at  $x > 0.08$  is suppressed and we can expect a high- $T_C$  in this case. However, it is noted that because the  $\text{Be}_N$  2p-states



**Figure 2.** Curie temperature versus Mn concentration. The Be concentration is chosen as 0 (dotted-circle curve),  $y = 0.48x$  (dashed-diamond curve) and  $y = 0.4x$ ,  $z = 0.05x$  (solid-triangle curve).

of down spins are located close by the Fermi level, the impurity band of down spins can be broadened and cross the Fermi level, resulting in a compensation of DOS at  $E_F$  and a decrease of  $T_C$  if the concentration of Be at the N site is higher than the value of  $z = 0.05x$  that we have chosen.

### 3. Conclusion

We have presented the results of calculations for the DOS and  $T_C$  in three cases of doping to predict how to achieve high  $T_C$  GaN-based DMS. The obtained results show an enhancement of  $T_C$  with the codoping method by which the volume expansion caused by Mn is compensated, and also the hole density is raised due to Be substituting for both cations and anions. It is suggested that since one can increase the hole density as well as the 3d-PDOS at Fermi level by codoping,  $T_C$  can be higher than room temperature for all Mn concentrations of  $x \geq 0.02$ .

### Acknowledgments

This research is supported by the Special Coordination Fund for Promoting Science and Technology from the Ministry of Education, Cultural, Sport, Science and Technology. We thank Professor Akai H (Osaka University) for providing the KKR-CPA package.

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