Vacancy-induced intrinsic $d^0$ ferromagnetism and photoluminescence in potassium doped ZnO nanowires

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Cation vacancy-induced $d^0$ room temperature ferromagnetism was observed in nonmagnetic potassium (K) doped ZnO nanowires (NWs) synthesized within the pores of the anodic aluminum oxide template. The ferromagnetic signature was found to be significantly enhanced in the K-doped ZnO NWs with respect to the pristine ZnO NWs. The photoluminescence studies clearly indicated the presence of a large concentration of zinc vacancies in the K-doped ZnO NWs. An interesting correlation between the saturation magnetization and green luminescence intensity with the increase of K-doping has suggested that the magnetic moment originates due to Zn vacancy defects. It is expected that the incorporation of K-related defects at the Zn site might promote the formation of zinc vacancies in the system and introduce holes to stabilize the hole-mediated room-temperature ferromagnetism. For the doped ZnO NWs the ferromagnetic response was found to be a maximum at an optimum K-concentration of 4 at. %. This study demonstrates that the ferromagnetism in ZnO can be tuned by controlling the cation vacancy-defects with the proper dopant in the host semiconductors.

I. INTRODUCTION

The idea of the manipulation of the spin and charge degree of freedom in a single material, namely, dilute magnetic semiconductors (DMS) by the introduction of transition metal (TM) ions replacing some host cations have been expected to be promising candidates for spintronic applications during recent decades. 1,2 The TM-doped wide bandgap metal oxide semiconductors, such as ZnO, SnO2, In2O3 etc, are anticipated to exhibit room temperature (RT) ferromagnetism (FM) and still, to date, the origin of magnetism in these TM-doped oxide semiconductors is controversial 4-12 and the existing theories cannot provide satisfactory explanations to the observed phenomena. However, the observation of RTFM in pure HfO2 thin films by Venkatesan et al. 13 has opened up a new phenomenon, the so-called $d^0$ ferromagnetism (FM). Ferromagnetism is also reported in the pristine ZnO, TiO2, SnO2, Al2O3, and In2O3 oxide thin films and nanostructures. 14-20 The origin of FM has been attributed to the different structural defects present in these oxide semiconductors. Several reports have suggested that point defects can generate localized moments and mediate FM in such oxides. 21,22 The ab initio calculations performed by Pemmaraju et al. 23 for HfO2 and Elfimov et al. 24 for CaO indicated that the cationic vacancies can induce an almost localized magnetic moment on the oxygen atoms neighboring the vacancy. In contrast, the case of oxygen vacancy (anion vacancy) leads to the absence of a magnetic moment. The term $d^0$ FM suggests that the magnetism does not originate from partially filled $d$-orbitals but from $p$-electrons of neighboring cations adolescent to the cation vacancy.

Generally, ZnO nanostructures are enriched with different types of intrinsic point defects or lattice imperfections. The most common lattice defects in undoped and doped ZnO are zinc vacancies, oxygen vacancies, zinc interstitials, zinc antisites, oxygen interstitials, and oxygen antisites. 25 The generation of these defects depends upon the sample preparation conditions and on the type of the dopants used. Doping in ZnO can also lead to the formation of structural inhomogeneity. Some of the intrinsic defects or structural imperfections have a significant role in the magnetic origin of the ZnO nanostructures and thin films. The structural inhomogeneity, identified by the high resolution transmission electron microscopy experiments by Xing et al., 26 has been reported to enhance the magnetic signature of the Cu-doped ZnO NWs. Radovanovic et al. 27 have demonstrated the robust ferromagnetism in Ni-doped ZnO nanocrystals based on the increase of domain volume and interfacial defects between the nanocrystals. Recently, Xu et al. 28 have reported intrinsic RTFM in boron-doped ZnO thin films, where the magnetic moment is induced in the nearest neighbor site to B-$V_{Zn}$ pairs. A first-principles density functional theory based calculation has shown that each Zn vacancy ($V_{Zn}$) carries a moment of $\sim$1.33 $\mu_B$. 29 However, several researchers have also demonstrated the FM in the ZnO thin films and nanostructures based on the oxygen vacancies ($V_O$). 16,17,20 Based on extensive first-principles calculations, Wang et al. 30 have demonstrated that the magnetism in ZnO thin films and NWs are due to $V_{Zn}$ instead of $V_O$. However, a proper understanding of defect-induced $d^0$ FM in ZnO is very important in order to fabricate ZnO-based DMSs. Recently, it has been reported that doping of proper elements in ZnO thin films can stabilize $V_{Zn}$ and introduces holes at the same time to generate ferromagnetic ordering in the material. 29,31 Similarly, the incorporation of cation vacancies in
ZnO nanostructures to control FM is also very exciting from the perspective of practical applications. However, to date, most of the reports are focused on the $d^0$ magnetism in ZnO thin films; whereas the cation vacancy induced magnetism in ZnO nanostructures has not been investigated properly, to the best of our knowledge. Therefore, in this work we have synthesized pure ZnO nanowires (NWs) and potassium (K)-doped ZnO NWs by an easy wet chemical template assisted route using nanoporous anodic aluminum oxide (AAO) as a template. The as-prepared undoped ZnO NWs exhibit RTFM and it is found that the FM signature increases with the increase of K-doping, having the maximum magnetization ($0.38 \text{ emu/g}$) for 4 at. % K-doping. The origin of the enhanced magnetization in K-doped ZnO NWs has been investigated by correlating the photoluminescence (PL) results with magnetic measurements. The studies indicate that the enhanced magnetic signature in K-doped ZnO NWs is because of the formation of large members of $V_{Zn}$. Hence, the possibility of tailoring the magnetic properties in K-doped ZnO NWs by controlling the cation vacancies by choosing the proper dopant can open new horizons in spintronics.

II. EXPERIMENTAL METHODS

A self-ordered nanoporous AAO template was synthesized by a controlled two-step electrochemical anodization of high purity (99.998%) aluminum foil. The overall experimental process is summarized here as the details of the experimental methods have been elaborated upon elsewhere. The annealed aluminum foil surface was polished electrochemically by using an electropolishing setup. Electropolishing was carried out at a dc bias of 40 V for 20 s using an acidic electrolyte. Afterwards, the foil was degreased in acetone for the necessary cleaning and the mirrorlike electro-polished face of the Al foil was anodized in a conventional two electrode electrochemical bath. A solution of 3 wt. % oxalic acid was used as the electrolyte, where the electro-polished Al foil and Cu plate were used as the anode and cathode, respectively. Anodization was carried out at a temperature of 10°C by maintaining a constant current density of 200 A m$^{-2}$ by varying the dc anodization voltage between 50–55 V. After the first-stage anodization for 20 min, the as-grown oxide layer was carefully removed by chemical etching using 60 wt. % H$_3$PO$_4$, 28 wt. % H$_2$SO$_4$, and a 12 wt. % HNO$_3$ acid mixture. An Al foil containing the footprints of the pore bottom grown after the first-step of the anodization was re-anodized for the second time for 2 h to synthesize a highly ordered AAO template of uniform pore diameter. For better pore mouth opening and pore rounding, the as-prepared template was immersed in 10 wt. % H$_3$PO$_4$ acid solutions for 25 min. The AAO template was cleaned several times in double-distilled water to remove the soluble acidic inclusions to prepare as the host for the NWs growth.

Arrays of un-doped and K-doped ZnO NWs were fabricated within the pores of the AAO by employing a simple wet chemical method. The arrays of ZnO NWs were grown by dipping the template into a saturated 0.1 M solution of Zn(CH$_3$COOH)$_2$$\cdot$2 H$_2$O prepared in ethanol followed by drying and annealing of the template as reported in our previous work. For the fabrication of various (2, 4, and 8 at. %) K-doped ZnO NWs, a selective amount of potassium acetate was added into the zinc acetate solution in appropriate ratios. The AAO templates were immersed in these mixed solutions and left for five days so that the solution could reach inside the nanopores. The surface of the templates were washed very carefully in order to remove the mixed acetate solution from the surface. All of the templates dipped in the zinc acetate and the mixed acetate solution were dried at room temperature and annealed in air at 450°C for 2 h. During annealing, the arrays of ZnO NWs and K-doped ZnO NWs were grown within the pores of the AAO through the decomposition of the acetate salts.

To study the morphology of the NWs by field emission scanning electron microscope (FESEM), the AAO template was partially dissolved in a 2 M NaOH solution to release the NWs. X-ray diffraction (XRD) was used to obtain the crystallographic information for the template embedded un-doped and K-doped ZnO NWs. The chemical composition of the NWs was determined by energy dispersive x-ray (EDAX) analysis. Room temperature PL measurements of the template embedded NWs were conducted by using a spectrofluorometer (Horiba Jobin Yvon, Fluorolog-3), having a Xe lamp source with an excitation wavelength of 330 nm. Magnetic measurements of the aligned arrays of template embedded un-doped and K-doped ZnO NWs were carried out by using a vibrating sample magnetometer (VSM, Lakeshore, model 7144) in the temperature range of 80 to 550 K.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the representative low magnification FESEM image of the bunch of as prepared 4 at. % K-doped ZnO NWs released from the AAO template. The high magnification FESEM image of the same is shown in Fig. 1(b), and the inset of Fig. 1(b) shows the FESEM image of a single broken NW. The diameter of the NWs is about 50 nm, which is found to be very close to the diameter of the pores of the AAO. The elemental composition obtained from the EDAX analysis indicates the presence of 1.94, 3.89, and 7.09 at. % K in the ZnO NWs host and it is less than the nominal percentages of 2, 4, and 8, respectively. The XRD patterns of the un-doped and the K-doped ZnO NWs are shown in Fig. 2(a), which indicates a hexagonal wurtzite crystal structure.
structure of ZnO. All of the NWs are found to be polycrystalline in nature. The lattice parameters of the hexagonal unit cell for all the K-doped ZnO NWs are estimated using Bragg’s diffraction law. The variation of lattice parameters ($a$- and $c$-parameters) are plotted in Fig. 2(b). Both the lattice parameters, $a$ and $c$, are found to increase almost linearly with K concentration, which ascertains the substitution of K ions replacing Zn ions. However, a close inspection shows that the change in the $c$-parameter is more rapid than the $a$-parameter. The result indicates that the majority of K ions are substituted along the $c$-axis of the unit cell resulting in significant elongation of the $c$-parameter. Consequently, an expansion of the lattice volume ($a^2c$) is also observed in K-doped ZnO NWs [see the inset of Fig. 2(b)]. The strong diffraction peaks at the 2$\theta$ values of 38.48 and 44.84 appear from the electro-polished Al substrate underneath the AAO template.

The PL spectroscopy has been extensively employed to study the optical properties of a variety of ZnO nanostructures. Generally, at room temperature ZnO nanostructures exhibit luminescence in the UV region as well as in the blue-green, green, and yellow regions because of the crystalline defects and/or impurities. The RT PL spectra of the as-prepared pure- and K-doped ZnO NWs embedded in the AAO are shown in Fig. 3. The AAO template itself provides a broad blue emission band centered around 430 nm [inset of Fig. 3(a)] due to the presence of oxygen vacancy defects as previously reported. Both the un-doped and K-doped ZnO NWs provide a UV emission near 383 nm, which is attributed to the near bandedge (NBE) electronic transition and/or the free exciton recombination through an exciton–exciton collision process. It is evident from Fig. 3(b) that K-doping results in the enhancement of the intensity of the NBE UV emission in doped NWs and the 4% K-doped ZnO NWs provide the strongest UV luminescence.

The un-doped and K-doped ZnO NWs exhibit a green deep level emission peak centered at 510 nm (2.43 eV). However, the reason behind the origin of this well-known green emission of ZnO nanostructures is still highly controversial and it is believed that it may not be due to a single source of luminescence. Among several hypotheses, the oxygen vacancy related defects are considered to be the cause of the visible green emission, but other in-depth investigations have revealed that the green luminescence of ZnO nanostructures is mainly related to the $V_{Zn}$ rather than the $V_{O}$ defects. Generally, oxygen vacancy defect related luminescence bands for ZnO nanostructures appear at a higher wavelength region. However, it is reported that the $V_{Zn}$ have low formation energy under n-type conditions, which indicates that the annealing conducted in air in order to synthesize the ZnO NWs promotes the formation of $V_{Zn}$. Therefore, the ZnO NWs grown in this work should contain a large amount of $V_{Zn}$ defects. Recently, Yi et al. demonstrated that the formation energy of the $V_{Zn}$ decreases because of Li doping in the ZnO matrix and hence the $V_{Zn}$ are stabilized. However, it is interesting to note that in our experiment, the intensity of the green luminescence peak of the pure ZnO NWs is significantly low. Whereas, the green emission peak becomes sharper in the case of the K-doped ZnO NWs and its intensity increases with the increase of the K concentration up to 4% K-doping. These results indicate that the K-doping in ZnO NWs promotes the formation of more $V_{Zn}$ and hence helps the NWs to exhibit enhanced luminescence in the green wavelength region. Therefore, correlating our experimental evidence with these reports, we
believe that the green emission of the un-doped and K-doped ZnO NWs can be ascribed to the $V_{\text{Zn}}$.

The K-doped ZnO NWs also exhibit few intense blue-green emission peaks at 450, 467, and 481 nm, which are not present in the PL spectrum of the un-doped ZnO NWs. Therefore, the blue-green emissions of the K-doped ZnO NWs might have originated from different K-defects such as K substitutional ($K_{\text{Zn}}$) and/or K interstitials ($K_i$). The 4% K-doped NWs exhibit the strongest blue-green luminescence characteristics among all the K-doped ZnO NW samples. Therefore, K-doping in ZnO NWs leads to significant enhancement in the PL.

Figure 4(a) and (b) show the hysteresis (M-H) loops of the un-doped and K-doped ZnO NWs at 300 and 80 K, respectively. The magnetic signal of the aligned ZnO NWs was obtained after subtracting the magnetic response of the AAO template. It is evident that the un-doped ZnO NWs exhibit FM at RT and at low temperature. Interestingly, the ferromagnetic response is found to be enhanced after K-doping in the ZnO NWs. The magnetic moment initially increases with the increase of K concentration up to 4% K-doping and then decreases with further doping. The maximum saturation magnetization ($M_s$) of 0.38 emu/g has been obtained for 4% K-doped ZnO NWs at $T = 300$ K. Figure 4(c) shows the temperature dependence of magnetization of the un-doped and 4% K-doped ZnO NWs. The Curie temperature ($T_C$) of un-doped and 4% K-doped ZnO NWs is 386 and 516 K, respectively. The variation of $T_C$ with the K concentration is shown in Fig. 4(d). It is found that the $T_C$ of the K-doped ZnO NWs also increases with the increase of the K concentration in ZnO NWs up to 4% K-doping and then decreases with further doping, which follows the similar trend of the saturation magnetization. Therefore, an optimum K concentration of 4% can be defined, where the ferromagnetic properties of K-doped ZnO NWs became strongest.

Here, we demonstrate that the presence of the FM in the pristine ZnO NWs is because of the $V_{\text{Zn}}$ defect. This kind of cation vacancy defect can grow in the ZnO NWs during its fabrication through annealing at high temperature under an oxygen rich condition and their signature is also confirmed from the PL measurements. However, in ZnO, $V_{\text{O}}$ is also a common defect and the $V_{\text{O}}$ clusters can also introduce moments in the system. Therefore, the influence of $V_{\text{O}}$ clusters in the FM of ZnO NWs is also considerable. Although in our experiment, the major contribution to the ferromagnetic response of the un-doped ZnO NWs is believed to be due to the presence of cation vacancies ($V_{\text{Zn}}$). However, an interesting correlation between the nature of $M_s$ and the green emission intensity ($I_G$) should be noted for the K-doped ZnO NWs, where both of them increase with the increase of the K concentration in ZnO up to 4% K-doping (see Fig. 5). Additionally, earlier PL measurements of K-doped ZnO NWs (see Fig. 3) indicate that a significant amount of $K_{\text{Zn}}$ and/or $K_i$ defects are also present in the NWs. Therefore, the formation of defect combinations such as $K_{\text{Zn}}$ and/or $K_i$ lowers the formation energy of each Zn vacancy and hence stabilizes $V_{\text{Zn}}$, which is similar to the case of Li-doped ZnO thin films. With the increase of K-doping in ZnO NWs, more $K_{\text{Zn}}$ and/or $K_i$ defects are likely to form, and hence more $V_{\text{Zn}}$ are grown (this is evident from the PL spectra), which results in an enhancement in the magnetization. The 4% K-doped ZnO NWs have the largest amount of K related defects and $V_{\text{Zn}}$ defects. Therefore, the 4% K-doped ZnO NWs exhibit the strongest FM signature because of the large concentration of $V_{\text{Zn}}$ defects. However, the decrease of the $V_{\text{Zn}}$ concentration and consequently, the
magnetization beyond 4% K-doping suggests that the formation of \( V_{\text{Zn}} \) depends upon the relative abundance of \( K_{\text{Zn}} \) and/or \( K_i \) defects. The observed correlation between the \( V_{\text{Zn}} \) concentration and saturation magnetization fairly suggest that the origin of the FM is related to \( V_{\text{Zn}} \). Some important estimated values for the K-doped ZnO NWs are summarized in Table I.

For further confirmation of the magnetic origin in K-doped ZnO NWs, we have re-annealed the as-grown NWs again at 500°C in O\(_2\) atmosphere and measured the M-H loops. Figure 6 shows the RT M-H loops for the as-grown and annealed 4 and 8% K-doped ZnO NWs. It is interesting to note that the magnetization has been slightly enhanced for both samples after annealing in \( O_2 \) atmosphere. Børseth et al.\(^{42}\) have demonstrated that the high temperature annealing in the O-rich condition decreases the \( V_{\text{O}} \) concentration, whereas the \( V_{\text{Zn}} \) concentration may increase. If the origin of the magnetic moment were associated with \( V_{\text{O}} \) defects, then the magnetization should have been decreased after annealing in the \( O_2 \) atmosphere. But that has not happened in our experiment. Therefore, the enhancement of magnetization in annealed NWs certainly confirms the \( V_{\text{Zn}} \) induced ferromagnetism in K-doped ZnO NWs.

It has been reported that the magnetic moment in the ZnO NWs originates from unpaired \( 2p \) electrons of the O atom in the immediate vicinity of \( V_{\text{Zn}} \).\(^{30}\) The substitutional defects (such as \( K_{\text{Zn}} \)) originated due to the doping of group-I elements and the \( V_{\text{Zn}} \) introduced holes in the system. The ferromagnetic interaction can be mediated by these holes between the magnetic moments of \( V_{\text{Zn}} \) to have a long range interaction.\(^{29}\) The model proposed by Bouzerer and Ziman\(^{21}\) have shown the dependency of a vacancy-induced local magnetic moment and magnetic coupling required by long-range ordering described via a single correlated band of oxygen orbitals with additional random potentials. This type of potential arises due to the substitutional defects and density of vacancies present in the matrix. For a small potential, antiferromagnetic nearest neighbor coupling exists. As the potential increases, ferromagnetic coupling begins to dominate but with a further increase of potential or substitutional defect concentration, coupling becomes antiferromagnetic again. They predicted that a well-defined region of potential, defect concentration, and carrier density exists where ferromagnetism with high temperature is possible with a few percentages of vacancies or substitutional defects like Li, Na, K, etc. Beyond the optimum window of defect concentration, the magnetic moment along with \( T_c \) vanishes, as the magnetic couplings are destroyed by Rudermann-Kittel-Kasuya-Yosida type oscillations or antiferromagnetic superexchange. Here in our study, we also have observed that at up to 4%}

![FIG. 5.](image1) **FIG. 5.** (Color online) Change in saturation magnetization \( (M_s) \) and relative intensity of green emission peak \( (I_G) \) of the NWs with K-concentration.

![TABLE I. Typical estimated values of lattice volumes, relative intensity of green emission \( (I_G) \) of PL spectra, saturation magnetization \( (M_s) \), coercivity \( (H_c) \), retentivity \( (M_r) \), and Curie temperature \( (T_c) \) for un-doped and K-doped ZnO NWs.**

<table>
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<th>NWs</th>
<th>K % (nominal) (at. %)</th>
<th>Lattice volume (Å(^3))</th>
<th>Relative Intensity of green emission peak ( I_G ) (a.u.)</th>
<th>Saturation magnetization ( M_s ) (emu/g) at 300 K</th>
<th>Coercivity ( H_c ) (Oe)</th>
<th>Retentivity ( M_r ) (emu/g)</th>
<th>Curie temperature ( T_c ) (K)</th>
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<td>0.10</td>
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<td>0.03</td>
<td>386</td>
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<td>0.22</td>
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<td>0.02</td>
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<tr>
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<td>99</td>
<td>0.05</td>
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<tr>
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<td>0.81</td>
<td>0.24</td>
<td>124</td>
<td>0.04</td>
<td>471</td>
</tr>
</tbody>
</table>

![FIG. 6.](image2) **FIG. 6.** (Color online) RT M-H loop for the as-prepared and annealed (a) 4% and (b) 8% K-doped ZnO NWs in O-rich atmosphere.
K-doping the $T_c$ increases and then decreases upon further K-doping. With the increase of K-doping in ZnO, the hole concentration should increase in the matrix and after an optimum hole concentration the ferromagnetic ordering is gradually destroyed resulting in a decrease of the magnetic moment and $T_c$ beyond 4% K-doping in the ZnO NWs.

**IV. CONCLUSIONS**

In summary, un-doped and K-doped ZnO NWs have been successfully fabricated within the pores of the AAO template by employing a simple wet chemical template assisted route. The K-doped ZnO NWs exhibit enhanced RT luminescence in the green and blue-green regions, which are ascribed to the $V_{Zn}$ and K-related defects, respectively. The expansion of the lattice volume with K-doping in ZnO NWs supports the substitution of K ions replacing the Zn ions of the host. Both the un-doped and K-doped ZnO NWs exhibit $d^0$ RTFM. The ferromagnetic response of the ZnO NWs is found to be enhanced upon K-doping. Magnetization increases proportionally with K-doping up to a certain K concentration (4%) and decreases upon further K-doping. The experimental results suggest that the sample preparation condition should have an important influence on its optical and magnetic characteristics. The observed correlation between the green emission peak intensity ($I_{green}$) and saturation magnetization ($M_s$) suggests that the Zn vacancy-induced $d^0$ ferromagnetism in ZnO NWs can be stabilized by K-doping. The study indicates the possibility of tailoring the magnetic properties of ZnO nanostructures by controlling the cation vacancies using a suitable dopant and can be found to be very promising to fabricate ZnO-based defect-engineered DMS devices.

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