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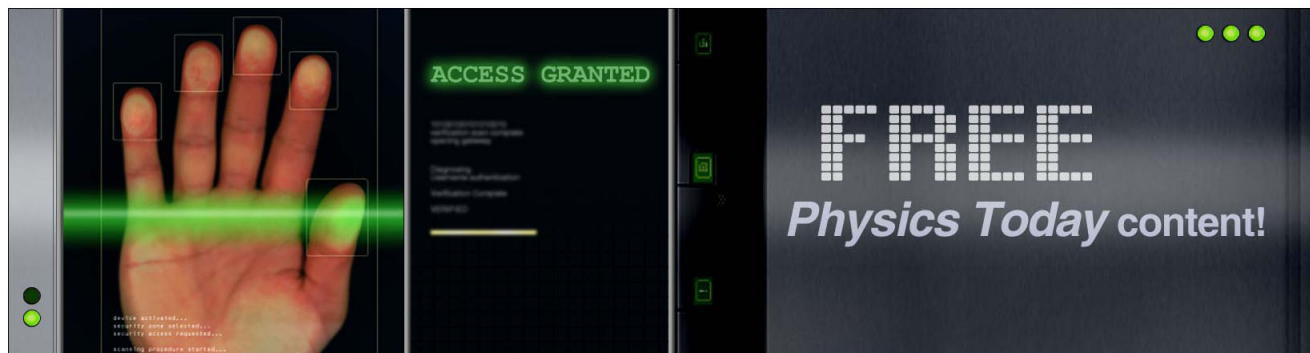
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## ADVERTISEMENT



## Strong ferromagnetism in Pt-coated ZnCoO: The role of interstitial hydrogen

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We observed strong ferromagnetism in ZnCoO as a result of high concentration hydrogen absorption. Coating ZnCoO with Pt layer, and ensuing hydrogen treatment with a high isostatic pressure resulted in a highly increased carrier concentration of  $10^{21}/\text{cm}^3$ . This hydrogen treatment induced a strong ferromagnetism at low temperature that turned to superparamagnetism at about 140 K. We performed density functional method computations and found that the interstitial H dopants promote the ferromagnetic ordering between scattered Co dopants. On the other hand, interstitial hydrogen can decrease the magnetic exchange energy of Co-H-Co complexes, leading to a reduction in the blocking temperature. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4705304>]

The manipulation of spin ordering in ferromagnetic dopants is interesting with respect to spin transport and the development of “spintronic” (spin-based electronic) devices. Although many semiconductors exhibiting high-temperature ferromagnetism have been identified, the microscopic origin of their magnetic properties is still rather controversial, particularly in the II-VI semiconductors such as ZnO. One of the most promising materials in this field is zinc cobalt oxide (ZnCoO or ZCO). The observation of ferromagnetism in ZCO at room temperature has intrigued many researchers.<sup>1–3</sup> The phases of metallic nanoclusters may have contributed to the observed magnetism. However, the potential sources of ferromagnetism without such metallic secondary phases are interesting and warrant an in-depth study. Despite several experimental and theoretical studies, the origin of room temperature ferromagnetism in ZCO and related transition metal-doped zinc oxides is still debated. Reports have suggested that Zn interstitials or an inhomogeneous distribution of transition metal ions can lead to ferromagnetism.<sup>4–8</sup>

We and others proposed and demonstrated experimentally that ferromagnetism in ZCO is closely related to the hydrogen concentration.<sup>9–12</sup> Hydrogen dopants preferentially sit on the bond centers between Zn and O and Co and O, and act as shallow donors, generating electron carriers without affecting the spin ordering. When Co atoms are doped at high concentrations ( $>7\%$ ), a significant amount forms dimer structures. In this case, another favorable site for H atoms is between Co-Co dimers, forming a bridge bond. The Co-H-Co complex has been shown to exhibit stable ferromagnetism.<sup>9,12</sup> Hydrogen dopants likely have various effects, depending on their configuration and concentration. Furthermore, the effect of hydrogen doped at higher concentrations has not been studied. Thus, the response of ZCO

to concentrated hydrogen dopants requires further investigation.

In the present work, we fabricated ZCO thin films (190 nm thick) by radio-frequency (RF) magnetron sputtering in Ar gas at 350 °C. A 10 nm Pt layer was deposited on each ZCO film by sputtering at room temperature, and hydrogen treatment was performed for 10 h at 300 °C under 500 bar in an Ar:H<sub>2</sub> (9:1 wt. %) gas mixture using hot isostatic pressure (HIP). The presence of a Pt layer has been suggested to promote hydrogen permeation into the ZCO film through the spillover effect.<sup>13,14</sup> We consistently observed an unprecedented carrier concentration. We also detected strong ferromagnetism and discuss the origin in relation to the configuration of hydrogen dopants.

Figure 1(a) shows a schematic of the hydrogenation of Pt-coated ZCO films. Hydrogen concentrations in the samples were measured by secondary ion mass spectrometry (SIMS) depth profiles, as shown in Fig. 1(b). The pure ZCO (black) showed a uniform hydrogen concentration throughout the sample; the concentration was consistent with natural contamination. When the ZCO film was hydrogenated using HIP (ZCO:H, red), the hydrogen concentration increased uniformly throughout the sample. We also measured the hydrogen concentration after coating the ZCO sample with Pt (green). When Pt-coated ZCO was treated with HIP (Pt/ZCO:H, blue), the hydrogen concentration increased substantially across the entire film. This can be attributed to the spillover phenomena of activated hydrogen atoms on the surface of the Pt layer.<sup>13,14</sup> We also measured the carrier density using Hall measurements and found that the room-temperature carrier density was about  $10^{21}/\text{cm}^3$ , which is 10 000 times greater than that of pure ZCO ( $10^{17}/\text{cm}^3$ ).

Currently, it has been reported that the carrier concentration can be enhanced via the large piezoelectric effect in ZnO.<sup>15,16</sup> We have examined the possibility of the piezo-induced effect for our sample and have found from our

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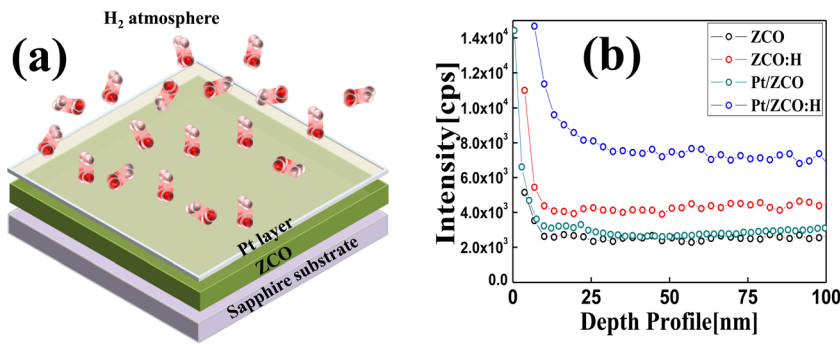


FIG. 1. (a) Hydrogenation process to Pt coated ZCO on sapphire substrate. (b) Hydrogen profile using SIMS depth profile for ZCO and Pt/ZCO before and after hydrogen treatment using HIP.

previous experimental studies using XRD, synchrotron-scattering, neutron-scattering, and maximum entropy method (MEM) that the changes in the lattice constant by hydrogen injection were very small (strain: 0.02% (a-axis), 0.03% (c-axis)).<sup>10,12</sup> Although this small change in the lattice constant might contribute to a local lattice distortion in ZnCoO:H, it is unlikely that it could induce a large change in the carrier concentration.

We investigated the magnetic properties of our ZCO films (with and without hydrogen treatment) using a superconducting quantum interference device (SQUID) at low temperature (10 K) and room temperature, as shown in Figs. 2(a) and 2(b), respectively. Without hydrogen treatment, the ZCO and Pt/ZCO films exhibited paramagnetic behavior, and the hysteresis was negligible at both temperatures. At low temperature, the hydrogenated samples [ZCO:H and Pt/ZCO:H in Fig. 2(a)] showed clear ferromagnetic hysteresis curves. The remnant magnetization of Pt/ZCO:H (0.424) was 5 and 10 times greater than those of ZCO:H (0.075) and plasma-treated ZCO without a Pt coating (0.040), respectively.<sup>17</sup> The hysteresis of

hydrogen-treated ZCO was reduced at room temperature [ZCO:H in Fig. 2(b)]. The hydrogen-treated Pt-coated sample (Pt/ZCO:H) showed a different temperature profile. At low temperature, Pt/ZCO:H exhibited large ferromagnetism, as shown in Fig. 2(a). At temperatures above 140 K, the ferromagnetism of Pt/ZCO:H rapidly disappeared, transitioning to superparamagnetic behavior. Figure 2(b) shows the superparamagnetic behavior of Pt/ZCO:H, with negligible hysteresis at room temperature.

We measured temperature-dependent magnetization (M-T) curves of the samples at a field strength of 50 Oe under field-cooling (FC) and zero-field-cooling (ZFC) conditions. No difference was observed in the M-T curves of Pt/ZCO under FC and ZFC conditions, as shown in Fig. 3(a). However, the M-T curves of Pt/ZCO:H showed a blocking temperature ( $T_B$ ) at 140 K, and the FC and ZFC curves are almost superimposed from 150 to 300 K [Fig. 3(b)]. To verify whether the observed ferromagnetism originated from secondary phases (e.g., Co clusters), we intentionally thermally annealed the Pt/ZCO:H samples under vacuum to eject hydrogen. As shown in Fig. 3(c), after annealing at 500 °C, the magnetism of the dehydrogenated Pt/ZCO:H was clearly diminished and reverted to the value of the Pt/ZCO sample before hydrogenation [compare Figs. 3(d)–3(f)]. This supports the hypothesis that the magnetization did not originate from the metal cluster. We investigated the depth profiles of Pt/ZCO by x-ray photoelectron spectroscopy (XPS) before and after heat treatment under high pressure HIP in order to better understand the change of state of the Pt layer before and after HIP treatment, and to check for Pt-derived secondary phase formation.

In Figure 4, the Pt layer was only detected below a thickness of 10 nm at the ZCO surface in both samples, suggesting that Pt had not penetrated the ZCO thin film after HIP treatment. The peaks in Figure 4(a) correspond to the signal of Pt(OH)<sub>2</sub>, which is converted to Pt after HIP treatment (Figure 4(b)). This result suggests that the Pt layer on ZCO attracts H from the atmosphere to form Pt(OH)<sub>2</sub>. Hydrogen-doped Pt was then injected into the ZCO thin film by HIP treatment without any decomposition of the Pt layer. Secondary structural phases, such as Pt-capped Co nanoparticles, were not detected.<sup>18</sup>

To explain our experimental observations, we performed first-principles density functional calculations using the plane-wave self-consistent field (PWSCF) package.<sup>19</sup> We used Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and ultrasoft pseudopotentials. This implies that the contribution from a Pt-derived structures (e.g., Pt-capped

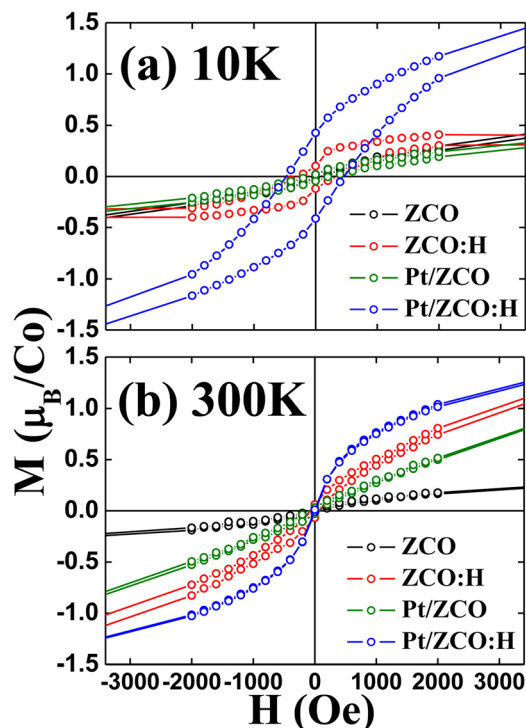


FIG. 2. The M-H curves obtained from SQUID for ZCO and Pt coated ZCO before and after hydrogen treatment using HIP (a) at 10 K and (b) at room temperature.

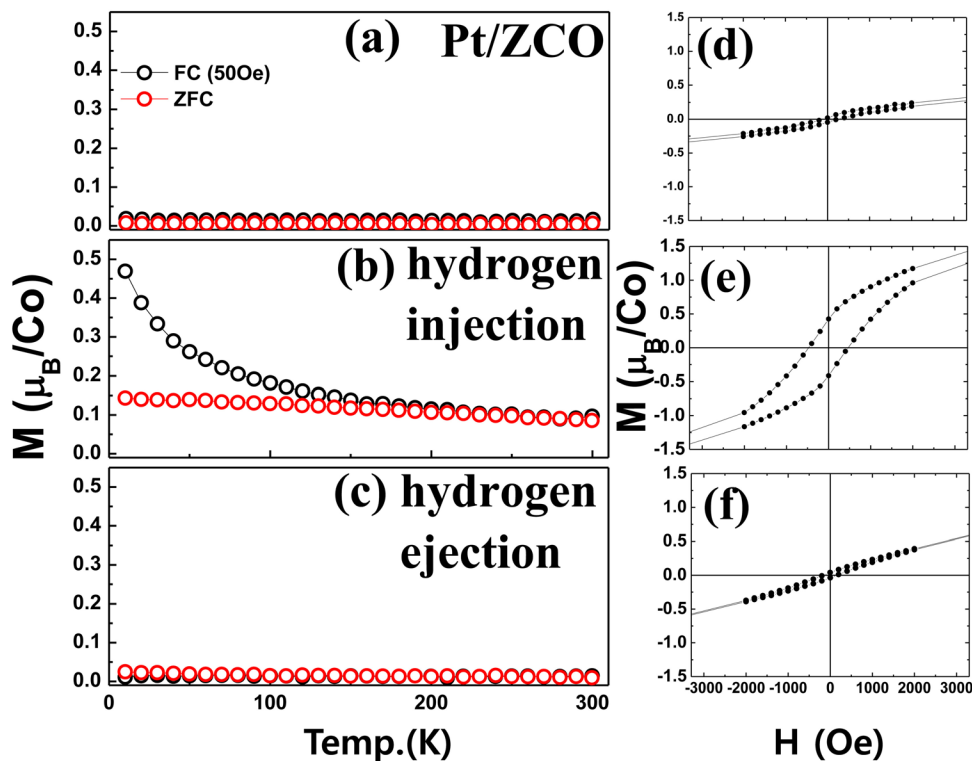


FIG. 3. The  $M$  vs  $T$  curves under field cooling and zero field cooling of (a) as-grown, (b) after hydrogen treatment, and (c) after dehydrogenation process of Pt/ZCO:H. The  $M$ - $H$  curves obtained from SQUID for (d) as-grown, (e) after hydrogen treatment, and (f) after dehydrogenation process at 10 K.

Co nanoparticles) is negligible.<sup>20,21</sup> The plane-wave basis set with a kinetic energy cutoff of 40 Ry was used throughout the calculations. A wurtzite supercell of 551 and 221 Monkhorst-Pack  $k$ -point grids was used. Two Co atoms were located at Zn sites in the computational unit cell, and five hydrogen atoms were placed in the interstitial sites. Even though hydrogen atoms are most stable at bond-center sites (Zn-O or Co-O), they have no magnetic effect. Upon HIP treatment, a substantial amount of hydrogen is thought to occupy the interstitial sites. Therefore, we considered the contribution from hydrogen atoms in the interstitial sites in our theoretical model.

The stability of ferromagnetic ordering can be estimated by the magnetic exchange energy (MEE), defined as

$E_{EX} = E_{AF} - E_{FM}$ . We found that the MEE of the Co-H-Co was 405 meV without interstitial hydrogen dopants in our computational scheme. This is consistent with the value reported previously.<sup>9</sup> When the hydrogen atoms were placed in the interstitial sites around the Co-H-Co units, the MEE was reduced to 146 meV, as shown in Fig. 4(a). However, for Co pairs at a longer distance, the presence of interstitial hydrogen atoms amplified the ferromagnetism. Figure 4(b) shows that the spin density of interstitial hydrogen atoms interconnects the tails of spin densities from the Co pair in the next nearest-neighbor sites. The value of the MEE in this case was 25 meV. Note that the MEE was negligible for the same Co-Co configuration without interstitial H atoms. This result implies that interstitial hydrogen atoms can mediate ferromagnetic ordering not only between nearest-neighbor Co-Co pairs but also between separated pairs. These results explain the amplified ferromagnetism at low temperature.

Experimental observations showed that the Pt coating combined with HIP treatment increased ferromagnetism in ZCO films (Pt/ZCO:H) at low temperature (10 K). However, Pt/ZCO:H had a lower  $T_B$  (140 K) than the sample without Pt. The observed behaviors were reversible upon repeated heating and cooling. This is also consistent with the computational results, as described above. Our theoretical model suggests that the presence of interstitial H atoms increases the likelihood of ferromagnetic ordering between Co pairs at distances longer than that of Co-H-Co (Fig. 5). This means that more Co atoms can connect ferromagnetically, leading to increased remnant magnetization. Such weak mediation by interstitial H atoms for separated Co pairs is effective only at low temperature. Our computational results show that, in the presence of interstitial H atoms, the MEE of Co-H-Co units decreases, and their ferromagnetism is likely to be disturbed at lower temperature.

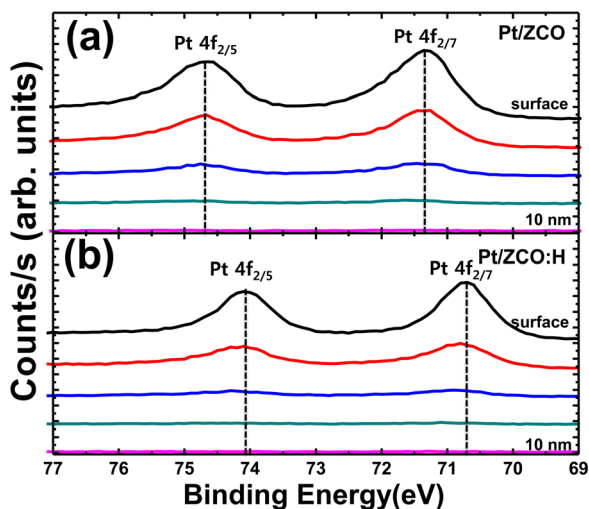


FIG. 4. XPS depth profile of Pt 4f of Pt/ZCO (a) before and (b) after hydrogenation by HIP treatment.

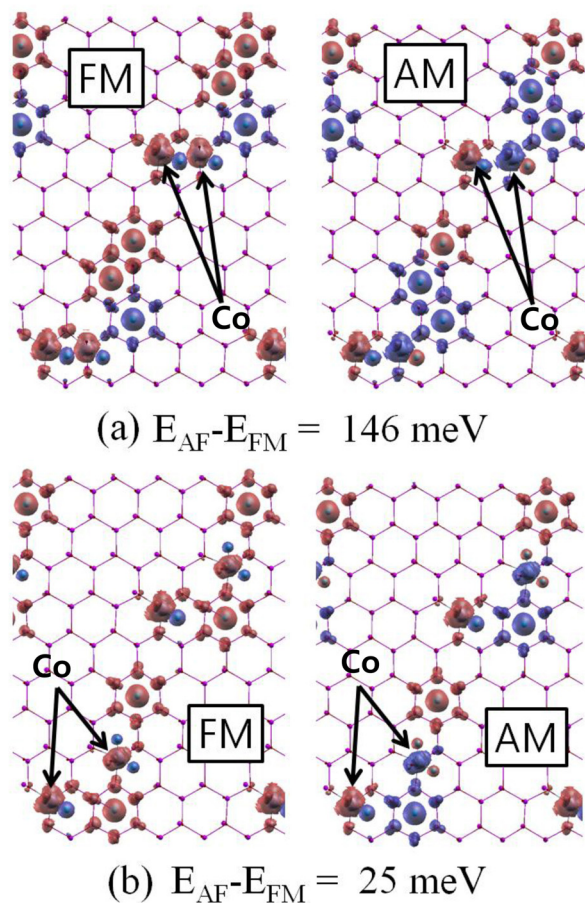


FIG. 5. Spin densities of model geometries. (a) Nearest neighbor Co dimers in the form of Co-H-Co. (b) Two Co atoms on the next nearest neighbor sites. Red and blue balloons represent majority and minority spin densities. The atoms in hexagon centers are interstitial hydrogen atoms. Arrows in (a) and (b) indicates the positions of the Co atoms.

In summary, we observed that a Pt coating combined with HIP treatment strongly enhances ferromagnetism in ZCO films. Upon heating above 140 K, the Pt coated ZCO:H showed superparamagnetic behavior, whereas the uncoated ZCO:H retained marginal ferromagnetism even at room temperature. This is thought to be induced by Co-H-Co complexes. After annealing at 500 °C, the magnetism of both samples disappeared. We performed first-principles density functional method simulations and showed that the presence of interstitial H atoms, as a result of increased hydrogen concentration, can mediate long-range magnetic ordering between separated Co atoms. Such weak mediation is effective only at low temperature. Our computational results

showed that due to interstitial H atoms, the ferromagnetism induced by Co-H-Co complexes is likely to be disturbed at lower temperature.

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